

MONOGRAPHS ON INDUSTRIAL CHEMISTRY

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LEAD

ITS OCCURRENCE IN NATURE, THE MODES OF ITS
EXTRACTION, ITS PROPERTIES AND USES, WITH
SOME ACCOUNT OF ITS PRINCIPAL COMPOUNDS

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PREFACE.

THIS book aims at giving, within somewhat restricted limits, the broad outline of the chemistry of lead. To that end, technical detail has been subordinated and though the endeavour has been made to portray modern practice, many of the older processes have received attention, either by reason of their intrinsic chemical interest, or as the forerunners of modern methods. For the same purpose, also, stress has been laid on the historical aspect of the subject and on the mutual relations of lead and its compounds in nature.

The state of our knowledge of the chemistry of lead is frankly unsatisfactory and reflects credit neither on the chemist nor on the scientific metallurgist. Many practical processes of fundamental importance are now obsolescent or extinct and the opportunity of presenting them in their true chemical bearing has passed. The scientific fate of their modern substitutes appears to evoke but little interest and it is tolerably certain that some of these will pass away before they have received adequate interpretation and their end will possibly be hastened by reason of this. In a word, the development of the subject is still, as in the past, empirical.

It must be confessed that the attempt to elucidate the chemistry of some of the operations described in this book has been disappointing to the author, who has had to content himself, in many cases, rather with a statement, or a partial one, of the problem than with an explanation. In the present state of our knowledge, however, the critical discussion and definition of these problems is urgently needed as a preliminary step towards their solution.

The author wishes to acknowledge his indebtedness to many other writers on this subject — to Percy, whose great work is still, after half a century, authoritative and makes such an impression of freshness and vigour; to Hofman, Schnabel and Collins, whose books cover every aspect of the metallurgy of the metal and bring the story up to the present day. Those who seek further information concerning modern American methods of smelting

and fuller references to the extensive writings on the subject may be referred to Hofman's *Metallurgy of Lead*.

He would also tender his grateful thanks to several friends who have helped in various ways:— to his colleague, Mr. W.G. Waddell, M.A. who has read the proof-sheets of the first chapter; to Mr. A. Short, M.Sc., F.I.C. Works Manager of the Howdon Desilverising Works of Messrs. Cookson and Co. Ltd. who has given him much information on desilverising and smelting; and to Mr. J. B. Duncan, M.Sc., F.I.C. Works Manager of the Hayhole White Lead and Lead Oxide Works, of the same firm, who has read the proof-sheets on white lead and, in the course of many discussions, has not only supplied valuable information on the preparation of white lead, but also materially moulded the author's views on the chemistry of the subject.

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CHAPTER I

HISTORY OF LEAD

The excavations of modern archaeologists have disclosed many leaden objects of great antiquity. Small statues, chiefly of Osiris and Anubis have been found in Egyptian tombs dating from the time of Rameses III. (1200 B.C.) and slabs and ornamental objects have been unearthed from Nineveh, Daphnae, Mycenae and Tiryns. Probably the earliest specimen of lead known dates from 3000 B.C. and is a figure found in the temple of Osiris at Abydos and now preserved in the British Museum.

The first documentary evidence of the metal occurs in the early books of the Bible in the account of the booty taken from the Midianites. "Only the gold and the silver, the brass (copper), the iron, the tin and the lead, everything that may abide the fire, ye shall make it go through the fire, and it shall be clean." (*Numbers XXXI. 22.*) This extract is of particular interest, in that mention is made of all the metals known to the ancients; quicksilver, though known well to the Greeks, being discovered at a much later date.

Concerning the Biblical tin and lead much discussion has arisen as to the significance of the Hebrew words *bedil* and *oferet*. In the old Greek testaments, *bedil* is translated by *χασιτερος* and *oferet* by *μόλυβδος*, and these Greek words are rendered in the Vulgate by *stannum* and *plumbum* respectively. There are, however, discrepancies in the rendering of these words and difficulties arise especially as to the meaning of *bedil*, which is used in the plural in the sense of dross (*Isaiah I. 25*) and is mentioned as the material of a

plummet (*Zechariah* IV. 10). Thus it has been questioned whether the Midianites in the time of Moses were acquainted with tin, though it is certain there is much bronze of great antiquity. The Greeks were undoubtedly cognisant of the metal which was named in the time of Aristotle (384 to 322 B.C.) Celtic or Tyrian tin (*τὸν κασσίτερον τὸν ζέκτιζόν*), and it was identified by Pliny, under the name of *cassiteros*, with *plumbum candidum*, which is indubitably tin. Thus Pliny states: *Sequitur natura plumbi, cujus duo genera, nigrum atque candidum. Pretiosissimum candidum, a Gracis appellatum cassiteron* (*Hist. Nat.*, 34. 47). Pliny's *stannum*, however, is certainly not tin but the *IFerk* (silver-lead alloy) of the German metallurgists, as maintained by Agricola and most subsequent writers, and it was not until the fourth century A.D. that *plumbum candidum* was rendered by *stannum* and the latter word thus became general for tin.¹

It is apparent that the early workers and writers on the metals encountered much difficulty in the identification of some of their preparations, and it is not surprising that lead should have been confused with tin, and each with alloys and smelting products. Other biblical references, relating especially to cupellation and refining of lead, occur in the books of the Old Testament and some of these will be mentioned in connexion with these processes.

Many of the Greek and Latin authors refer to lead and its compounds, either specifically as matters of scientific interest, or incidentally as articles of common use, the properties of which have left their impress on the social customs of the age.

The most important of the former class are the Greek writers Theophrastus (371—288 B.C.), fragments of whose writings only (e. g. *περὶ λίθων*) survive, and Dioscorides (1st Century A.D.), whose great *Materia Medica* is a well of

¹ For a full discussion of this problem c. H. Kopp, *Geschichte der Chemie*, Vol. 4, 125, and J. Beckmann, *History of Inventions, Discoveries and Origins*. Trans. Johnston, 1846.

information on the methods of preparation and the medicinal uses of numerous mineral and vegetable drugs. The Latin writers include Vitruvius (*ca.* 25 B.C.), who describes in his work *De Architectura* many of the materials used in building, and above all the elder Pliny (23—79 A.D.), whose *Historia Naturalis* is a compendium of the scientific knowledge of his age. Occasional notes of scientific interest bearing on this subject are to be found in the writings of many of the philosophers and historians.

From the time of Galen (2nd. Century A.D.), there is little authentic information on the subject until about the 11th. Century, when the names of Geber, Theophilus and Eraclius, followed by Roger Bacon, Albertus Magnus and Basil Valentine, stand out with some prominence, and this period is closed and the modern era inaugurated in 1556 by the great work of Agricola, *De re metallica*, in which, for the first time, is given a complete account of the metallurgy of lead and the other important metals.¹) Other works of this period which deserve mention are *Le la Pirotechnia* by Biringuccio, 1546; *Aula Subterranea* by Lazarus Erockern, 1574, translated and amplified by Sir John Pettus and published under the title *Fleta Minor*, 1683, and the *Britannia Baconica* of Joshua Childrey, 1661. In the following historical sketch, the various aspects of the subject will be considered separately and the endeavour will be made to do fuller justice to the knowledge of the classical authors than in usually the case.

MINING AND SMELTING

Mining was introduced into Greece and Spain by the Phoenicians, a great trading race of Semitic origin which came from the shores of the Red Sea, Persian Gulf and

¹ This work has been admirably translated by H. C. Hoover and L. H. Hoover, London, 1912. Many notes of great historical interest are added by the translators, to which the author would acknowledge his indebtedness.

Indian Ocean. They were followed by the Carthaginians, whose importance in the metal world is apparent from the Biblical reference to the glory and riches of Tyre: „With silver, iron, tin and lead they traded in thy fairs“ (Ezekiel XXVII. 12).

The Phoenicians are said to have controlled the silver-lead mines of Spain as early as the 12th. Century B.C., and the value of these mines is frequently lauded by the ancient writers. Polybius (204—125 B.C.), states that the mines at Carthagera employed 40,000 men and yielded to the Romans 25,000 drachmae daily. The mines at Attica played an important part in the life of Greece. Xenophon, writing in the 4th. Century B.C., on the means of improving the revenues of the state, affirms that they were worked in very ancient times. The fleet which conquered the Persians at Salamis (480 B.C.), was built from the revenues of these mines. The re-opening of the old workings at Laurium within recent years has confirmed the statements as to their extent and importance, and afforded evidence of smelting at a low temperature and by forced draught, and also of cupellation of the argentiferous lead.

The Phoenicians traded with Britain, bartering earthenware, salt and copper, for lead, tin and hides. Though Cicero states that there is no silver in Britain—*etiam illum jam cognitum est, neque argenti scripulum esse ullum in illa insula* (*Epist. ad Att.* IV. 16)—Strabo and others affirm its presence, and as the only possible source of the silver is lead ore, this would appear to indicate that the process of cupellation had been discovered, or at least put into operation, in the meanwhile. Pliny ¹⁾ (Lib. 34. Cap. 17) particularly notes the ease with which lead ore is found and won in Britain, compared with Spain and Gaul—in *Britannia summo terrae corio adeo large—*

¹ All references to Pliny are from the *Natural History*. In future, only the numbers of the book and chapter will be given. References to Dioscorides are chiefly from Book 5 of the *Materia Medica*; only the chapters, in Roman numerals, are cited in such cases.

and it is certain that the Romans wrought and smelted lead ore very extensively in this country.

Most local historians of lead-mining districts are inclined to date the opening of their mines to Roman times, often on insufficient grounds; but there is ample evidence that lead mines were worked by the Romans in the Mendips, Somersetshire, Shropshire, Derbyshire, and in various parts of Wales. Roman lamps of lead have been found in the Mendips; their implements at Shelve in Shropshire;¹⁾ remains of smelting furnaces at Ebchester in Durham²⁾ and many lead pigs (*massae plumbei*) either near the mines and boles, or primitive hearths, or on the great trade routes. These pigs resemble the modern ones in shape, weight and marking. The usual weight is about 168 lbs. (1.5 cwt.), or some fraction of this (127 or 83 lbs.); occasionally they are made of many layers, the result of separate teemings—a practice used in the Peak in the time of Childrey (*Brit. Bacon.* 1661)—and they are generally stamped with the name of the reigning Emperor. The earliest date from the time of Claudius (44—48 A.D.) and they range therefrom to the reign of Hadrian (117—138 A.D.).³⁾ On the Continent pigs of Roman lead (*Bleiklumpfen*, *Saumons de Plomb*) have been found in Germany, France, Spain, Sardinia and Italy. Some of these are thought to be derived from Shropshire.

Little is known of the state of mining in Britain after the withdrawal of the Romans, though, as lead articles (e. g. coffins) of Saxon age have been found, it is evident that the industry was not for long extinct, if indeed there was any break in the continuity. The Derbyshire mines were worked in the 8th Century and there is a record in Domesday Book (1081) of a lead mine at Crice (Crich?). Authentic records of mines and of grants to miners exist from the 13th Century, but the great development of lead mining dates from the

1 Murchison, *Silurian System*, 279.

2 J. C. Bruce, *Roman Wall*, 433.

3 For a list of these see A. Way, *Arch. Journ.*, 1859, **16**, 22; 1866, **23**, 277.

reign of Queen Elizabeth, who brought over Daniel Hochstetter and Thomas Thurland from Germany. In a short time (1565) practically all the mines of England and Wales except those of tin and copper in Cornwall, were controlled by the German miners. Since these days, mining in Britain has had a chequered career. In 1839 more lead was produced in Britain than in the rest of Europe. The high-water mark of output was in 1856, when 353 mines were working and the production of lead was 73,129 tons.

Concerning the methods of dressing lead (and other) ores, there are some scattered references in the older authors, from which it is clear that hand-picking, crushing in stone mortars and washing were employed, but it was not until Agricola's time that detailed accounts of these processes are given. To the same author we must look for the first recognition of roasting as a metallurgical process of great importance, for the reasons that it facilitated the breaking up of hard ores before smelting and „that the fatty things, that is to say, sulphur, bitumen, orpiment or realgar may be consumed". The stamp-mill was invented about the same time (16th Century).

Of the appliances used in smelting, probably the most anciently known are the bellows, which seems to have been invented by the Egyptians. There is a reference to it in *Jeremiah* VI. 29.—"the bellows are burned, the lead is consumed in the fire, the founder melteth in vain." Little is known about ancient smelting furnaces. We learn from Strabo¹) that in Spain the silver-lead furnaces were lofty, "in order that the vapour which is dense and pestilent may be raised and carried off". Pliny speaks of firehearth, pillars and arches, and Dioscorides of dust chambers for the collection of pompholyx (zinc oxide, etc.).

The primitive forms in this country were wind-furnaces (boles) placed in a favourable position with respect to the

¹ *Geography*. Lib. III., Cap. 2, § 8. Hamilton and Falconer's edition.

prevailing winds. These were supplanted in time by slag-mills and hearths built on the plan of a smith's forge.¹⁾ Reverberatory furnaces are stated by Schlüter to have been invented by Wright in 1698 and used for smelting copper ores in Flintshire, though the invention is claimed by Becher, and one, fired with wood is described by Alonzo Barba as early as 1640. Reverberatories were introduced into Kalst-edge in Derbyshire for smelting lead ores in 1747 and speedily supplanted the ore-hearth for that purpose, for they allowed of the use of coal as fuel, were not so detrimental to the health of the furnace-men and made it possible to use the belland or slime ore. The recovery of the belland in Derbyshire by buddling dates from the introduction of reverberatories.²⁾

In the Alston district, reverberatories did not succeed in supplanting ore-hearths. Their application to the preliminary roasting (flash-roast) of ores to be used in the ore-hearth process dates from 1810.³⁾ The reverberatory method was never much used in America, apparently owing to lack of skilled labour. In Missouri, 56 furnaces were in use in 1877, but only 4 in 1914. The methods employed in the Mississippi valley in 1880, and the percentage of ore smelted by each are; ore hearth, 62.5; blast furnace, 19.3; reverberatory furnace (Flintshire and Air Furnace), 18.2.⁴⁾

Charcoal, wood and peat were the fuels used in smelting almost until the eighteenth century, and the drain upon the wood supplies of countries like England was consequently serious and led to wholesale deforestation. Holinshed speaks of lead mines in Wales (Comerswith) „which endured until all the wood was consumed in smelting”. The frequent

1 Martin, *Phil. Trans.*, 1729, 407; also J. Glanvil, *ibid.* 1688, 770.

2 J. Farey, *General View of the Agriculture and Minerals of Derbyshire*, 1815.

3 *Voyage Métallurgique en Angleterre*. Dufrénoy, Elie de Beaumont, Coste et Perdonnet. Paris, 1839. (2nd. ed.)

4 For earlier methods used in the Lower Mississippi see H. Garlich, *Min and Scient. Press*, 1917, 315

occurrence of Forest as a place-name in lead-mining districts where now are bare fells is, partly at least, to be ascribed to the consumption of wood in the industry. In the acquisition of wood for smelting purposes, the law greatly favoured the smelter. The substitution of coal for wood in smelting dates from the patent granted to Viscount Grandison, 1678, for smelting lead ore with sea coal in reverberatory furnaces. A little later, Oct. 4. 1692, the London Lead Company, formerly the Quaker Company, subsequently the Governor and Company, obtained their charter for smelting lead ore with coal. This famous company, which operated continuously until 1905, bears on its arms the inscription, „The Arms of the Corporation for Smelting Lead with Pitcoal and Seacoal“, and beneath, the motto „Spectatur in Igne“—it is tested in the fire.¹⁾

CUPELLATION AND REFINING

The Biblical writers seem to have been greatly impressed by the operations of cupellation and refining, a fact easy to understand from the striking nature of the phenomena and their application in the moral sphere, as well as from the practical importance of the processes, since most, if not all, of the silver of antiquity was won from silver-bearing lead. We read in *Ezekiel* (XXII. 18.), „The house of Israel is to me become dross; all they are brass, and tin, and iron, and lead, in the midst of the furnace, they are even the dross of silver.“ In *Malachi* (III. 2.) the angel is compared to a refiner's fire; other references to refining are to be found in the *Psalms* (XII. 6.) and *Proverbs* (XXII. 3.; XXV. 4.).

The preparation of gold concentrates by crushing and washing and the treatment of these in a furnace with lead (along with salt, tin and barley bran) for five days and nights is described by Agatharcides in the second century B.C., the account being preserved in the writings of Diodorus Siculus. The operation was termed ὀβερζα, and the purified gold,

¹ W. Wallace, *Alston Moor*. 1890

ὑβρεῶνον χρυσίου.¹) Strabo refers to the refining of silver by means of lead.²)

In a celebrated passage, Pliny (34, 47.) describes apparently the smelting of argentiferous lead ore, the cupellation of the work-lead and the revivification of the litharge.

Ejus qui primus fuit in fornacibus liquor, stannum appellatur; qui secundus, argentum: quod remansit in fornacibus galena, quae est tertia portio additae venae. Haec rursus conflata dat nigrum plumbum deductis partibus nonis duabus.

According to this, the first furnace-product is stannum—obviously our work-lead. This [on cupellation in another furnace] yields silver and the third product is 'galena'. This 'galena' on remelting [and reduction] gives lead, with a loss of two ninths and is evidently litharge.³) The statement of quantitative results at this early period is of considerable interest. According to Kopp, the converse phenomenon, viz: gain in weight attending the dressing of a metal is not mentioned by any of the ancient writers, though known to Geber. As the loss on reduction of the litharge is 22.2 p.c. and 7.2 p.c. is due to removal of oxygen, the difference, 15 p.c. must be ascribed to volatilisation and working-loss, if it be granted that Pliny's figure has any quantitative significance.

Pliny refers more specifically to cupellation in another passage (33, 31). *Et eodem opere ignium descendit pars in plumbum, argentum autem superne innatat, ut oleum aquis* (By the agency of fire part [of the ore] is thrown down as lead [litharge] on which the silver floats like oil on water). H. C. Hoover and L. H. Hoover propose a transposition in this extract in accordance with specific gravities, though it seems possible that Pliny refers to the appearance of the silver button near the end of the cupellation-process.

1 Kopp, II. 37.

2 Strabo, *Geo. Lib.* II, 221.

3 For a critical review of this passage see Beckmann, *op. cit.* II. 211.

The refining of gold by melting with lead is mentioned by Pliny as a remarkable fact—*ut purgetur, cum plumbo coqui* (33, 19).

It is evident that the Romans desilverised lead in Britain, for many of the lead-pigs which have been unearthed bear the inscription EX ARG., EX ARGENT or LVT EX ARG. In the last, LVT is probably a contraction of *lutum*, washed, and the inscription may thus be rendered 'purified from silver', that is, desilverised.

There is but little information about cupellation from the time of Pliny until the twelfth century. Geber's account of the process is almost modern and Theophilus mentions cupels of bone-ash and beech wood ash. Opinions concerning the nature of the process were naturally erroneous; thus, according to Kopp, Albertus Magnus held that the lead was volatilised—*Purificatur argentum in igne cum plumbo, et per ustionem exhalat plumbum et separantur sordes ab argento*. In the sixteenth century, Biringuccio describes it as a metallurgical process and Agricola gives a very full account with illustrations of the German furnace which is still in use; he is also aware of the fact that lead for assaying should be free from silver, like that from Villach in Carinthia.

About this time much English lead (and ore) was exported to the Continent for refining and the Dutch had a high reputation in this art. In 1679, the value of the silver in English lead ore varied from £2 to £35 a ton and the lead was not thought to be worth refining unless the silver from one ton was worth £8.10.0.¹) A century later, refining was profitable when the lead carried about 9 ozs. of silver per ton. Watson²) gives some interesting details of refining at Holywell. The charge of 60 cwts. of lead from the Isle of Man yielded 60 ozs. of silver and 58 cwts. of litharge and the latter on reduction gave 52 cwts. of lead. The loss of lead is thus 8 cwts. on a 3 ton charge, whereas the Dutch are

• 1 G. Plattes, *A Discovery of Subterranean Treasure*, 1679.

2 R. Watson, *Chemical Essays*, 1789.

said to have lost only 6 cwts. for the same amount of charge. The ignorance and lack of skill of English smelters and refiners is a constant cause of lamentation among the writers of this period. Thus Thomas Bushell, who established the mint at Aberystwyth in 1637, complains "that through ignorance, the goodness of the ore is not known to the owner and so is transported to other nations for potter's ore, out of which strangers refine silver, to the great loss and prejudice of his Majesty's service".

The direct cupellation of silver-bearing lead was practised for possibly 4000 years, and it was not until 1833 that Pattinson invented his famous process whereby the silver is concentrated in a portion of the base metal and only the rich alloy is cupelled. This effected a great economy in fuel and labour, reduced considerably the loss of lead and made possible the profitable extraction of silver from poor silver-leads in which, formerly, the silver was of necessity lost.

THE USES OF LEAD IN ANCIENT TIMES

It seems strange to us that the ancients should have erred so greatly in appraising some of the simple physical properties of the metals. Even Pliny thought that gold was inferior to lead in respect to specific gravity and malleability (*facilitas*), for he says of gold: *Nec pondere, aut facilitate materiae praclatum est ceteris metallis, cum cedat per utrumque plumbo.* (33, 19.) Lucretius (*De Rerum Natura* V. 1241) falls into a similar error. In describing the discovery of metals by the burning of forest trees situated on ore deposits, he emphasizes the 'weight' of silver, though this is less than that of gold and lead.

*Quod superest, aes alque aurum ferrumque repertumst
Et simul argenti pondus plumbique potestas.*

The expression '*plumbique potestas*' is of some interest. It may be rendered 'lead with all its peculiar properties', or 'lead with its useful and unique qualities', and possibly refers to those phenomena of cupellation and refining which made so great an impression on the mind of antiquity.

Lead had many uses among the Greeks and Romans. In warfare it was used for sling-bolts (*glandes plumbeae*), oval in shape and pointed at both ends, and for tipping arrows (*plumbatae sagittae*); in civil life for toys, vases, tokens, market-weights, plummets, net-sinkers, coffins, reels, tablets and seals. Lead discs for drawing lines on parchment are mentioned by Pliny (33, 19).¹ Sheet lead was cast and water-pipes (*fistulae*) made from it by bending the sheet round a rod and soldering the edges (Pliny, 34, 17). The proper length for piping was 10 feet and precise data are given both by Pliny and Vitruvius connecting the circumference and the weight. Those five fingers in circumference (termed *quinaria*) weigh 60 lbs.; those eight fingers (*octonaria*) weigh 100 lbs.; ten fingers (*denaria*), 120 lbs., and so on in proportion. For high pressures 5-finger piping is recommended. The use of lead pipes for conveying water was also common among the Arabians, and it is recorded that the fourth Spanish Caliph, Abdurrahman (850 A.D.), brought water to Cordova through lead pipes.

The Romans were acquainted with soldering and many surviving examples of their handiwork attest their skill in this art. Pliny states (33, 30 and 34, 47), that lead cannot be soldered without tin, or tin without lead, and neither without a flux (*sine oleo*). Two alloys are described, *argentarium*, containing equal proportions of each metal and *tertium*, containing twice as much lead as tin; the latter was used for soldering—*hoc fistulae solidantur* (34, 48). Both alloys were used as substitutes for *stannum* in the making of mirrors. The mediaeval practice of backing glass mirrors with lead or tin was possibly a survival or adaptation of this custom.

The use of lead, mentioned by Herodotus, in fixing iron clamps to the stone bridge of Nitocris in Babylon and for a similar purpose by Thucydides (I xciii. § 5), has its parallel in Britain at Cilurnum (Chollerford) on the Tyne.² and

¹ See also Catullus, xxii, 8.

² J. C. Bruce, *The Roman Wall*, 1867, 346.

seems to be referred to by Horace in his famous ode (I. 35).
Ad Fortunam:

Te semper anteit sacra Necessitas

Clavos trabales et cuneos manu

Gestans aëna, nec severus

Uncus abest, liquidumque plumbum.

Here is pictured stern Necessity preceding Fortune, bearing in her hands the symbols of inexorable doom, viz: spikes, wedges, the clamp and the molten lead to secure it.

Passing mention may be made here to some references in the Latin authors, as indicating the general appreciation at that time of the properties of lead. Thus Cicero jocularly, if scornfully, suggests the feeble character of a person by averring that he could be slain with a leaden sword (*plumbo gladio*). The metaphorical use of *plumbei* in the sense of 'stupid people' is also of interest in this connexion, while in the common association of the seven metals and planets, lead was paired with Saturn, the cold planet in contact with the frozen regions of the heavens, near the extremity of the universe (Vitruvius, Lib. 9 Cap. 4), and was represented by the symbol h , which is interpreted either as the scythe of Father Time or as a corruption of the first two letters of the word *Κρόνος* (Saturn).¹) It is of interest to note that the ancient Japanese also associated the five metals known to them, viz: gold, silver, copper, iron and tin, with the planets.²)

LITHARGE

This is described by Dioscorides under a number of names, some of which are transliterated by Pliny, who also copies largely the account of its preparation and properties and adds important, if somewhat confused, details. It is certain that some of the preparations mentioned by these authors are impure and they probably contained arsenate and antimonate of lead, and even lead sulphate, as well as the oxides of metals like tin, copper, etc.

¹ Beckmann, *op. cit.* Vol. II. 25.

² W. Gowland, *Journ. Inst. Metals*, 1910, IV. 4.

Dioscorides says of *λευδάργυρος* (CII) that one sort is made from sand (ἐκ . . . ἄμμου) which is called leady, another from silver, and a third from lead. The best is Attic, has a yellow colour and bears the name *chrysitis*; the next is Spanish, of silver colour and termed *argyritis*, and the poorest (*lauritis*) was made from silver and came from Puteoli, Campania and Sicily. Pliny adopts the first two names but calls the poorest *molybditis* (33, 35), so that it is doubtful whether this was derived 'from silver'. The method of preparation from leady sand (ore concentrates?) and sheet lead is by burning in a furnace, with or without the use of bellows.

The *molybdaena* of both authors agrees very closely with the above description. It is friable, of moderate weight, best in quality when gold-coloured and somewhat shining (*ἐπιστίλβουσα*) and free from metallic lead; it becomes reddish-yellow when ground and is found in furnaces of silver and gold, as well as in the native condition. Less well characterised are the *σκωρία ἀργύρου* of Dioscorides (CI), the *scoria argenti* or *spuma argenti* of Pliny (33, 35); *σκωρία μόλυβδου* (XCVII) or *scoria plumbi* (34, 51) and the *λίθος μόλυβδοειδής* (XCVIII) or *lapis plumbarius*, but there is little doubt that they all refer to preparations consisting partly of litharge. The *scoria argenti* was also called *ἡλκυσμα* (*helcysma*) and *ἐγκαυμα* (*encauma*), the first name being of especial interest as indicating the viscous nature of the molten litharge (ἔλκω, I drag). The production of litharge in the cupellation process is evidently referred to by Pliny in his description of the molten body flowing from the higher to the lower part of the furnace—*ex superiore catino defluens in inferiorem* (33, 35) and of the shaping of the material in tubular form by catching it on iron spits and twirling it in the flames, in order to reduce its weight—*ut sit modici ponderis*.

RED LEAD

Red lead is apparently first mentioned by Vitruvius (*De Architectura* VII. 12) who states that it is prepared by roasting white lead, which becomes converted thereby into *sandaraca*,

the product being superior to that procured from mines (orpiment?). Dioscorides (CIII) gives a similar method, the white lead being heated, with stirring, until the colour becomes like that of sandarach. As some call the red substance sandyx, it appears that a difference between red lead and orpiment was at least suspected. Pliny (34, 54 and 35, 20) refers to red lead as (*cerussa*) *usta*, repeats the method of preparation just given, and amplifies a story of Vitruvius that the discovery of red lead was accidental and the result of the burning of a house in the Piræus, in which was preserved a large jar of white lead cosmetic. His account of the substance is, however, very confused and it is evident that many red materials, e. g. *purpurea*, *rubrica* (oxide of iron), *cinnabaris* (the resin known as dragon's blood), 'marbled sil', the product of calcining ochre (*cremato sile marmoroso*), *minium secundarium* (found in lead and silver mines, also used in the preparation of quicksilver) and *sandaraca* (red orpiment) were all confounded with one another.

Dioscorides (Lib. V. CIX, CX.) was able to distinguish between dragon's blood or *cinnabaris* and true cinnabar or *minium* (*ἀἷμα* or *μίνιον*), for he states that quicksilver is made from the *minium* which is misnamed *cinnabaris* and the difference between the two bodies can only be discerned by heating, when the *minium* gives off a suffocating vapour. To prevent the inhaling of this, the operators covered their faces with bladders (an early mention of the gas-mask).

The common adulteration of true *minium* (vermilion or cinnabar) with red lead had one consequence of importance, in that the term *minium* was applied, in the course of time, to the adulterant. From the use of red lead in painting arose the term "miniature" which, in time, lost all trace of its association with red lead.

The preparation of red lead from litharge or metallic lead was discovered at a later date. According to Kopp, it was known to Geber, who writes—*plumbum adurit et fit minium*. Its chemical nature was for long hidden. Even Boyle writes (*Sceptical Chymist*, 1661) that "*minium* is but

lead powdered by the fire". In the hands of Scheele and Priestley, the compound attained some importance, for both prepared lead peroxide from it. Scheele by the action of chlorine, Priestley by means of nitric acid.

CARBONATES OF LEAD

A medicinal preparation used in plasters and as a hair-wash and eye-salve is described by Dioscorides (XCV) under the name of *ποηλεμένος μόλεβδος* and by Pliny (34, 50) as *plumbum lotum*. It is made by grinding water in a lead mortar with a lead pestle, or lead filings with rain water (*addita aqua coelesti*) in a stone mortar, sometimes with addition of vinegar, wine, fat or rose-leaves. The water darkens and becomes muddy, but after long grinding it whitens and resembles *psimythion* (white lead) *τὸ γὰρ ἐπὶ ἱκανὸν τριβόμενον γίνεται ψιμυθίου ὅμοιον*. The supernatant water is removed by straining through a linen sieve or by absorption with a sponge and the residue dried and made into pastilles. The accounts are free from ambiguity and the observations accurate; Pliny's mention of rain water is of considerable interest and there can be no doubt that the product was a basic carbonate of lead, resembling white lead.

There is probably no chemical preparation known to antiquity which has been so frequently and so accurately described as white lead, for as such we must identify the *psimythion*¹⁾ of the Greeks and the *cerussa* of the Romans. It is mentioned probably for the first time by Xenophon²⁾ (430—355 B.C.) who narrates a dialogue between Ischomachus and Socrates, in which the former describes how he instructed his wife in her duties and discountenanced her use of white lead and other cosmetics, on the grounds that it was displeasing to him and was an artifice easily discovered among those who live in intimacy.

1 The word is variously written *ψιμυθιον*, *ψιμυμθιον*, *ψιμυθιον*.

2 *Oeconomies*, cp. X. 7.

An excellent account of its preparation is given by Theophrastus¹⁾ (300 B.C.) which is worthy of being quoted in full.

"Lead ingots²⁾ are placed over vinegar in earthenware vessels. When the lead has thickened, which it does in ten days at the most, the mould-like material is scraped off and the operations are repeated until the lead is all corroded. The scrapings are then beaten in a mortar and boiled for some time, and the portion which settles out (*τὸ δ' ἔσχατον ἐκρυστάμενον*) is white lead."

The best white lead was made at Rhodes and the method used there is described by Vitruvius³⁾: "The Rhodians place, in the bottom of large vessels, a layer of twigs over which they pour vinegar, and on the twigs they lay masses of lead. The vessels are covered to prevent evaporation, and when after a certain time they are opened, the masses are found changed into cerussa."

Much the same method is described by Dioscorides (CIII.); he seems to recognise, however, the advantage of the vinegar and the lead not coming into contact, and this is achieved by placing the lead on a mat suspended by a stick in the middle of the jar. The product is strained and the sticky residue (*γλοιῶδες*) dried in the sun in summer, carefully over a fire in winter, ground in hand-mills and sifted. Pliny's account (34, 54) is evidently taken from Theophrastus and is of interest in that it definitely identifies psimythion with cerussa, adding the information that it is a product of lead-works—*psimithium quoque, hoc est cerussam, plumbariae dant officinae*.

Though in these early accounts of the preparation of white lead there is no recognition of the necessity of a source

1 *περὶ λίθων. Fragmenta*, II. 8, 56. F. Wimmer, Ed.

2 *μόλυβδος . . . ἐν πίθοις ἡλίκον πλίνθος*. Dioscorides uses a similar term, *μολυβδίνην πλίνθον* (CIII). Pliny (34, 54) states that the thinnest lead shavings are used — *fit autem ramentis plumbi tenuissimus*.

3 Lib. 7, Cap. 12. The extract is from Gwilt's translation.

of heat and carbon dioxide, yet the condition of reaction and the materials were such that these were not wanting, and the only matter for surprise is that the time usually mentioned, ten days, is so short. Probably the open nature of the whole process led to a speedy loss of vinegar and brought about thereby cessation of the corrosion—hence the frequent recommendation to repeat over and over again in order to use up the lead. The use of dung is mentioned by Galen (2nd century) and about ten centuries later by Theophilus and Eraclius, the former of whom gives what is practically the modern method of preparation. Alonso Barba¹) (1669) describes perforated plates of lead, his white lead (*albayalde*) being prepared by covering a vessel of strong vinegar with fine sheets of lead, full of small holes “and putting it into a hot muckhil and after twenty days standing there, rake out for use”. That both vinegar and a source of carbon dioxide are necessary was probably not always appreciated, for Sir John Pettus states: (*Fleta Minor*, 1683) that the best white lead is made of lead, “calcined with the vapours of vinegar, but the common way is by urine”; and again that white lead is a product from lead “corrupted with vinegar or urine”.

The Venetian process described by Vernatti in 1678, and the Dutch (said to have been introduced in 1622) by Jars in 1765 will be referred to later.

The question as to the chemical nature of white lead became an important problem in the 17th century. By most chemists (e.g. Lemery, Macquer) it was regarded as a derivative of lead and acetic acid, but Bergman²) recognised it as a carbonate (*haec nihil aliud est quam calx plumbi aerata*), since it dissolved in acids with effervescence, yielding a gas having the properties of fixed air, though, to his surprise, it was not soluble in carbonic acid. He is careful to state that he used a preparation free from chalk, the common adulteration with which was fully recognised by Basil

¹ *Arte de los Metales*. Translated by the Earl of Sandwich, 1669, under the title *The Art of Metals*.

² *Opuscula Physica et Chemica*, 1779.

Valentine, who in consequence recommended chemists to make their own white lead. Artists were also aware of the adulteration of this pigment, for Edward Norgate¹⁾ gives full instructions for grinding and washing white lead, which he found "the better for use and lease subject to mixture" than ceruse. Jars states (1765) that ceruse contains chalk but *Blanc de Plomb* is pure white lead.

White lead, like all lead compounds, was largely used by the ancients in medicine and elaborate instructions are given by Dioscorides for grinding, levigating and making up the preparations for medicinal uses. In his descriptions one may detect a rude effort toward characterisation of the bodies based on their obvious physical properties, such as colour, and their medicinal 'strength'. Pliny regarded it as the mildest of the lead preparations (*lenissima tantum ex omnibus*). It was employed for the removal of spots and blemishes, for healing scars and as eye-salves and hair-washes. Chaucer (1387) in the Prologue to the Canterbury Tales makes humorous reference to it when speaking of the facial imperfections of the Somnour:

Ther nas quik-silver, litarge, ne brimstoon,
 Boras, ceruce, ne oille of tartre noon,
 Ne oynement that wolde clense and byte,
 That him mighte helpen of his whelkes whyte,
 Nor of the knobbes sittinge on his chekes.

This is one of the early references to white lead in England, the earliest probably dating from 1274 when *albi plumbi* appears in an account rendered for the painting of the interior of the Painted Chamber.²⁾

White lead was largely used by the Greeks and Romans as a cosmetic, and the early mention of it by Xenophon (quoted above) is in this connexion. Ovid³⁾ gives a recipe

¹ *Miniatura, or the Art of Limning*, 1650; reprinted 1915. Ed. M. Hardie.

² C. A. Klein, *The Oil and Colour Trades Journal*, Dec. 6 and 13. 1913.

³ *De medicaminibus faciei*.

for making a face-wash consisting of cerussa, aphronitrum (sodium carbonate), lupins and sword-lily, blended with honey and yellow combs, etc. In Plautus,¹) a maid flatters her mistress by refusing to hand her white lead and rouge (*purpurisum*), explaining that on the same principle she will want to whiten ivory with ink: *Non istanc aetatem oportet pigmentum ullam attingere, Neque cerussam, neque melinum, neque aliam ullam offuciam.*

There is an interesting reference to the action of sunlight on white lead in Martial.²) The lady Maximina, who possesses only three teeth the colour of pitch, is admonished to refrain from laughing, and to dread it as much as Fabulla, with chalked face, does the rain, or Sabella, painted with white lead, the sun:

*quam cretata timet Fabulla nimbum,
cerussata timet Sabella solem.*

The same author (VII. 25.) refers to certain epigrams as more dazzling and spotless than a white-leaded skin—*cerussata candidiora cute.*

It has been argued from the extended use the ancients made of white lead as a cosmetic, that they were unaware of its poisonous properties, but these are specifically mentioned by all the great classical authorities. Pliny (35, 54) says that it is a deadly poison like the scum of silver (litharge), and Dioscorides³) prescribes as remedies honey-water, decoction of figs and mallow, hot milk and extract of burnt faggots. It seems probable that it was used by suicides, for Dioscorides⁴) states that it impossible to hide the taking of white lead, since it whitens the palate, gums, teeth and the interstices between the teeth. The poisonous nature of burnt lead (*μόλυβδος κεκαυμένης*) is also noted.

The preservation of iron from rusting by means of white

1 *Mostellaria*. Act. I. Sc. 3.

2 *Epigrammata*, Lib. II. XLI.

3 *Liber de Venenis eorumque precautionione et medicatione*. Cp 22.

4 See also: *De facile parabilibus simplicibusque medicamentis*, CLXIII.

lead (also of gypsum and tar) is noted by Pliny (34, 43), who further remarks that ships used to be painted in ancient times with a native cerussa found at Smyrna (35, 19), but that in his day all white lead was made from lead and vinegar—*nunc omnis ex plumbo et aceto fit*. Vitruvius also comments on the superiority of artificial white lead over that procured from mines.

There can be little doubt that the native cerussa of these authors was the mineral cerussite and that the similarity of this to white lead was recognised; the identity of the two bodies was maintained by Chas. Leigh,¹) long before Bergman had established the chemical nature of white lead, for, writing of the lead ores, he states that "the white ore is a natural ceruss".

It is doubtful whether the Romans used white lead for painting pictures. Davy²) could not detect any trace of it in the materials found in ancient baths, or in the scrapings from pictures.

LEAD SULPHIDE

The synthesis of this compound is described by Dioscorides (XCV), under the name of burnt lead (*μόλιβδος κεκαυμένος*), in this manner: "Place strips of lead, beaten out as thin as possible, in a new dish and sprinkle sulphur over them; add more lead and sulphur, and again more, until the dish is full: Kindle the mixture and stir it with a rod until it is completely reduced to ashes, which are like lead when well done."

Variations of this process in which lead filings are used, or in which barley or white lead are interspersed, are described, and also a method in which lead alone is used; in this case the operation is naturally difficult, for when the heat is severe, the ash assumes the colour of litharge. Pliny describes a similar process, the product being known as *plumbum ustum* (34, 50).

¹ *Nat. Hist. of Lancs. Cheshire and the Peak in Derbyshire*, 1700.

² *Phil. Trans.*, 1815, 97.

The name *galena* which we apply to the natural sulphide of lead, does not occur in Greek, despite its Greek appearance; like minium, it is probably of Spanish origin. It is, however, used by Pliny and in two senses; first, as identical, probably, with its present meaning, the material being found near veins of silver (*Galenam vocant, quae juxta argenti venas plerumque reperitur*) (33, 31); and secondly as synonymous with molybdaena (*Est et molybdaena quam alio loco galenam vocavimus, vena argenti plumbique communis... adhaerescit et auri et argenti fornacibus; hanc metallicam vocant* (34, 53).^{*} In the second case, galena has the characters of both the mineral and litharge, and its identification with molybdaena emphasises its relation to litharge and incidentally shows how confused Pliny was on this subject.¹)

Coming to more recent times, we find Agricola²) describing galena as composed of lead juice and the material which forms opaque stone; and again, of stone and lead containing some silver but not differing much from lead itself. The mineral was investigated with great skill and care by Dr. R. Watson.³) The specific gravity of different specimens was found to vary considerably and it is instructive to note that the discrepancies were ascribed either to differences in composition, to the presence of imperceptible spar, or to diversity in the size and configuration of the pores. The difficulty of obtaining the pure mineral encountered by Watson was evidently experienced by many of the chemists e.g. Kirwan, Proust, Davy, Berzelius, Wenzel, Doebereiner, Westrumb, who first analysed it (Vauquelin quotes analyses showing 15 to 36 p.c. of insoluble matter), and it has hampered the work of investigators in quite recent times.

¹ The confusion was greatly accentuated in the sixteenth and seventeenth centuries by the use of the old words *galena*, *molybdoïdes*, *molybdaena*, *lapis plumbarius*, etc., as well as new ones like *plumbago* and *grafio piombino* to connote both graphite and molybdenite. The true nature of these minerals was determined by Scheele in 1778; and the name graphite introduced by Werner in 1787.

² *De re metallica*, p. 51.

³ *Phil. Trans.* 1778, 73, 863. *Chemical Essays*, 1789. No. 7.

Kunkel (1743) had denied the existence of sulphur in galena, and the Derbyshire smelters are stated by Watson to have been totally unaware that their ore contained sulphur, but Watson affirmed its presence since the element was separated, along with the calx of lead (lead sulphate), by the action of nitric acid on the mineral. Distillation, however, did not yield sulphur, but only a small amount of liquid, and some black matter sublimed in the retort, which proved on microscopical examination to be "pure lead ore". Watson's chief conclusions are that galena contains lead, sulphur, a little water, and an air—this last a faulty inference from the behaviour of the mineral with nitric acid—and the volatility is established. "We may safely conclude" he says "that lead ore cannot be decomposed by the strongest fire in close vessels, but it may be sublimed in them".

Watson's further experiments are of fundamental importance in connexion with the explanation of smelting reactions. Though, as we have seen, lead ores (and undoubtedly galena was the chief of these) had been smelted successfully from the earliest times, little or nothing was known of the changes which took place in the process. The simple reduction of galena by means of iron was a novelty proposed by Boyle¹) and even this method could not be comprehended; much less then was the chance of explaining the complicated reactions taking place in hearths and reverberatories. Now Watson found that though no lead was produced on distilling galena in a closed retort, some metal was found when the retort cracked, so that "by a communication with the air through the crack, the ore was decomposed and thus both lead and scoria were formed".

An explanation of this all-important influence of air was soon offered by Mrs. Fulhame,²) and was based on her

¹ Watson may have been mindful of this when he suggested "fluxing sulphureous lead ore in conjunction with the scales or other refuse pieces of iron, or even with some sorts of iron ore".

² *An Essay on Combustion; with a view to a new Art of Dying and Painting, wherein the Phlogistic and Antiphlogistic Hypotheses are proved erroneous*, London 1794.

remarkable experiments on the influence of moisture upon chemical action. The air contains moisture and the galena was proved by Watson to yield a little water on distillation. It is to the action of this moisture, said Mrs. Fulhame, that we must ascribe the observed reduction of the mineral to metal. "The sulphur attracts the oxygen of the water, while the hydrogen of the latter unites in its nascent state to the oxygen of the metal and restores it to the metallic form."

Though we now know this explanation to be faulty, yet taken in conjunction with more modern work in this field, especially that of Baker, who succeeded in distilling dry sulphur trioxide upon quicklime, it suggests that moisture may have a considerable effect on the roasting of galena. It is quite likely that in its absence galena would be oxidised to litharge only, and it is even possible that this would not react with the unaltered, dry sulphide. With respect, however, to the main point, we may note that the necessity for the presence of air, and the absence of any "inflammable principle" were at first sight contrary to experience, and the name "air-reduction", given later to the process, well expresses the paradox. It was emphasized by Berthier, who brought about the reduction of galena to lead with such powerful oxidising agents as manganese dioxide and potassium nitrate (applied naturally in limited quantity), and whose work on the oxide, sulphide and sulphate of lead cleared the way for the interpretation of the air-reduction process.¹⁾

In the further development of this subject, special mention must be made of the work of Plattner,²⁾ in which many of the primary and secondary reactions taking place in the roasting of galena are worked out, e. g. the action of the oxides of sulphur on materials, either originally present in the charge or formed at some stage in the process. It is

1 P. Berthier, *Traité des Essais par la voie sèche*, Liège, 1847; *Ann. chim. phys.*, 1822, **20**, 275; 1826, **33**, 156; 1828, **39**, 262. Also Gay Lussac. *Ibid.*, 1836, **63**, 435.

2 C. F. Plattner, *Die metallurgischen Röstprozesse theoretisch behandelt*, Freiburg, 1865.

remarkable that Plattner, though he studied the action of sulphur dioxide on iron, copper and silver, should have overlooked its possible action on lead itself. This was reserved for Jenkins and Smith,¹) who thus made the very important discovery of the reversibility of the fundamental smelting reactions in the air-reduction process. The bearing of this work will be discussed in detail later.

CHAPTER II

OCCURRENCE OF LEAD. ORES, MINERALS AND LOCALITIES

THE MODE OF OCCURRENCE OF LEAD IN NATURE

Lead is an element which is widely distributed in nature, workable deposits being found in many countries and in all kinds of rocks, igneous and sedimentary, belonging to most of the geological epochs. Analyses which have been made in certain lead-raising areas indicate that the quantity of lead scattered throughout the country-rock of the district does not vary much from the average for the lithosphere (0.002 p.c.) as estimated by Clark and Washington. Thus, for British areas, Finlayson²) found an average of 0.0024 p.c. of lead in granite, diabase, ash, shale and limestone, the granites containing most (0.002—0.004 p.c.) and the limestones least (0.0005—0.0015 p.c.).

The chief mode of occurrence of lead ore is as a constituent of mineral veins, which are in the nature of fissures, often accompanied by faulting, filled with gangue minerals, metallic ores and fragments of the country rock; these veins are in places worked to great depth, though in other localities the lead may give out entirely or be replaced by other minerals in depth. They are often associated with igneous intrusions, in the form of dykes or sills, and occasionally they occur near the margins of large bosses of igneous rock.

¹ H. C. Jenkins, E. A. Smith. *Journ. Chem. Soc.*, 1897, **71**, 666.

² *Quart. Journ. Geol. Soc.*, 1910, **66**, 299.

When presumptive evidence of a genetic connexion exists between igneous activity and mineral deposition, the ores are spoken of as igno-genetic, and their source is ascribed to juvenile waters of magmatic origin. It has been stated that lead is more intimately connected with basic than with acidic rocks, but this relationship has not been substantiated. Igno-genetic lead ores are usually rich in silver. In Britain, the formation of such ores is referred by Finlayson to the Hercynian (Post-Carboniferous) epoch, the deepest zones of deposition being characterised by tin and tungsten (with some copper), the intermediate by copper (with some lead and zinc) and the upper zones by lead and zinc.

The rocks of Lower Carboniferous age in Britain are especially rich in lead ores, and when, as is usual, they consist of alternations of limestone, sandstone and shale, the thickness and the richness of the veins varies according to the nature of the rock through which they pass, the limestone being most favourable and the shale least. In the limestones too, particularly in the thick ones, occur those offshoots from the veins, known as flats, which follow roughly the bedding planes, sometimes opening out into caverns, and often prove extremely rich in ore. The veins shew a marked tendency to pinch out in igneous rocks, as has been often observed in the Great Whin Sill (intrusive diabase) of Northumberland, Durham and Cumberland and in the toadstones (contemporaneous lava) of Derbyshire, both of which beds occur in rocks of Lower Carboniferous age in highly mineralised districts. The older Palaeozoic rocks (Ordovician and Silurian) of Shropshire, several counties in Wales, the Isle of Man and the Leadhills in Scotland are also lead-bearing, and the metal can be occasionally extracted with profit from veins in granite, as, for example, in the Isle of Man and the Wicklow Hills.

At times, lead occurs in considerable quantity disseminated through sedimentary beds, giving rise to irregular-shaped ore-bodies, more or less horizontal, or at least defined by the bedding planes. Such deposits are supposed to have been

formed by the leaching-out of the metal from the surrounding country and its precipitation in favourable localities. They are termed sedi-genetic deposits and the lead ore they contain is usually poor in silver. The deposits of the Missouri region and those of Bleiberg and Mechernich in the Eifel are of this character. In England, there are similar occurrences of lead (and copper) in the Keuper sandstone (Upper Trias) of Alderley Edge, Cheshire and in the Bunter Conglomerate of Cannock Chase, but in neither case does the ore occur in large quantity.

The lead content of the ore as raised from the mine varies within very wide limits, examples of which will be given later; the average for American ores during the year 1914 was 5.7 p.c. The methods of dressing the ore do not concern us here; it will suffice to state that a concentrate of galena is delivered to the smelters. For the decade 1870—80, the average amount of lead in the concentrates from British mines was 75 p.c. (the extremes being 73 and 78.5 p.c.). As pure galena contains 86.6 p.c. of lead, this concentrate of average composition contains 86.6 p.c. of pure galena.

The common metal-associates of lead are iron, zinc and silver. Iron occurs as pyrites and siderite, and the weathering of these at the outcrop produces the rich ferruginous gossan, the 'iron hat' of the miners, which is held to betoken a rich vein. At Broken Hill, this iron (limonite) is highly mangani-ferous. In Weardale, siderite alternates with galena in such a manner that a mine may be worked at one place on a particular vein for lead, and at a closely-neighbouring place on the same vein for iron.

The association of zinc and lead is of chemical interest and great practical importance. Originally brought together by the similarity in properties of the sulphides, they may be separated in the zone of weathering by reason of their difference in stability towards weathering-agents and the difference in solubility of the oxidised products. Lead-bearing veins usually become richer in zinc as the depth increases. The difficulty of separating intimate mixtures of

galena and blende, and their comparative uselessness for the winning of either metal, has long been a matter of great economic importance; the problem of their separation would appear to be on the high road to solution as the result of the recent development of floatation-methods of dressing.

Silver is so frequently a constituent of lead ore, and lead under metallurgical conditions is such a good solvent for silver, that the two metals can hardly be considered apart. It is estimated that two-thirds of the silver produced in the world at the present day is derived from lead ores. In the United Kingdom the silver production in 1913 was 120 000 ozs., of which all but 4000 ozs., which were extracted from copper and zinc ores, was obtained from lead.

In galena, silver is frequently present in isomorphous mixture, as the sulphide argentite, and the loss of precious metal during the dressing of the ore is therefore proportional to the loss of lead. Should it occur in other form, such as the lighter and more brittle tetrahedrite, then the loss on dressing will be relatively greater than that of lead. Metallic silver, lining cleavage cracks in galena, may be met with in the higher levels, and enrichment of the ore in silver may occur in the cementation zone, owing to the precipitation of metallic silver, by means of sulphides, from solutions formed in the zone of active weathering. In the deep levels, below the cementation zone, metallic silver does not occur. Carbonate ores usually contain silver as the chloride, horn silver or cerargyrite, and gossan ores in general may show a concentration of silver, owing to the insolubility of its halides and their production from the original sulphide ores by weathering agents. The mineral associates of galena may also contain silver, and the amount may be greater or less than in the galena. Collins¹) quotes an example from Leadville where the galena contained 41.5 ozs. of silver per ton, and of the associated minerals, blende contained 94.5 and pyrites 4.5 ozs. per ton.

¹ *Metallurgy of Lead*, p. 22.

The amount of silver in lead ores varies within very wide limits. It is almost negligible (0.05 ozs. per ton) in the ores of Bleiberg, Carinthia, formerly famous for its virgin lead (*Jungfernblei*), and, on the other hand, ores such as those of Kongsberg and Schemnitz are so rich that they are rather to be classed as silver ores. A general estimate gives the ratio of lead to silver as 5000 to 1.¹) With respect to British ores, the variation in different localities is shown in the following table, in which are given the amounts of silver in ounces per ton of pig-lead from the ores smelted in 1847—one of the best years in the history of British lead-mining:

Shropshire—almost free.

Derbyshire—2.5 to 5.

Montgomeryshire Merionethshire 6.

Flintshire and Denbighshire 7.

Scotland 8.

Cumberland 9.

Ireland 10.

Durham, Northumberland and Westmorland 12.

Cardiganshire, Carmarthenshire and Carnarvonshire 15.

Cornwall 25.

Devonshire 40.

The Cornish and Devonshire ores have long been celebrated for their richness in silver, as much as 130 ozs. having been recorded in the pig-lead from Wheal Betsy, 120 from Beer Alston and 100 from the Garras mine. The lead smelted from Cardiganshire ores often ran 40—80 ozs. silver per ton.

The average silver-content of lead from British ores is estimated by Hunt as 5 ozs. per ton. For the year 1917, English lead yielded 4.88 ozs., Scottish 5.6 and Welsh, 10.7 ozs. of silver per ton.²) These estimates are somewhat low, since desilverising is not performed when the silver is

¹ Beyschlag, Vogt and Krusch, *The Deposits of the Useful Minerals and Rocks*, Trans. Truscott, 1914.

² Home Office Report on Mines and Quarries for 1917.

less in amount than 3 ozs. per ton, and a small amount (·25 ozs. per ton) of silver is left in the desilverised lead.

The silver content of pig-lead from British ores showed a considerable and almost continuous decrease for the decade 1870—80, the values for the individual years being 10·68, 11·03, 10·40, 9·79, 8·67, 8·48, 8·25, 8·10, 6·85, 6·46, 5·19 ozs. per ton.¹) It is doubtful whether this was entirely due to the working of deeper levels. Lodin²) has however shown that there is a clearly-marked dependence of silver-content on depth in the case of the Auvergne ores, the values (ozs. per ton in the lead extracted) for various depths being as follows:

Surface, 196; 40—60 metres, 163; 80—100 metres, 131; 180 metres, 116; 240 metres, 49.

The association of visible gold and galena is rare, but has been observed in specimens from Beresovsk and Argentina.

The gangue-minerals of lead-bearing veins show considerable variety. Calcite predominates and quartz is common, and there is a marked relation between these and the nature of the country rock in the immediate neighbourhood, limestone favouring the former and sandstone the latter. Fluorspar is abundant in the upper levels of Derbyshire, Weardale and Flintshire; in Derbyshire it passes in depth into calcite. In the Weardale mines, veins were formerly slit for galena, the ore being removed from the middle and the bulk of the fluorspar left; many of these mines have recently been reopened and worked primarily for fluorspar. When these veins are traced westward over the anticlinal axis of the Pennines, the fluorspar is found to be replaced by barytes. Barytes is a common gangue mineral in Shropshire.

LEAD, ORES AND MINERALS

Native lead has been reported from many localities, e.g. Alston, Madeira, Carthagena, but it is doubtful whether

¹ R. Hunt, *British Mining*, 1884, 836.

² Lodin, *Ann. des Mines*, 1892, 9, 1, 389.

all such occurrences are genuine. Specimens from the Harstig Mine showed cubical crystals of density 11.372 and gave an analysis 99.71 p.c. of the metal.

Of the many minerals containing lead, only three can be regarded as ores of the metal; these are galena, cerussite and anglesite.

Galena, PbS: This is by far the most important ore. It has many synonyms, such as galenite, blue lead ore, tessellated ore and dice ore. It belongs to the cubic system and usually crystallises in cubes or octohedrons or a combination of the two; the crystals are sometimes many inches in size and on occasion show evidences of corrosion. The colour is pure lead grey with a glimmering lustre; the specific gravity is 7.4—7.6 the melting point 1114°C , the hardness 2.5—2.75 and the solubility 3×10^{-4} grams per litre. The mineral shows true cleavage and breaks up into cubical fragments, hence the miner's name dice-ore.

It is evident from the general methods of occurrence and the nature of its vein-associates that galena is usually of hydrochemical origin, and this view is supported by many syntheses of the mineral which have been effected in the laboratory by the use of aqueous solutions. In this connexion, it is noteworthy that it has been observed in a stalactitic form in nature, and as an incrustation on fossil bones and on charcoal in old mines.¹) It is formed also from lead and sea-water, in presence of charcoal, which undoubtedly reduces the sulphates in sea-water to sulphides.²) Probably some similar reaction is the explanation of its formation in the old mines above-mentioned.

Cerussite, PbCO₃, otherwise known as lead earth, wheat-stone, white lead ore, has been found in large quantity at Laurium, Leadville, Carthagera, Linares, Broken Hill and other places celebrated for lead. It is naturally a gossan ore and produced from galena by the action of carbonated waters. When masses of this material occur in earthy form they con-

¹ Bischoff, *Chem. Geology*, Vol. 1, 42.

² A. Russell, *Min. Mag.*, 1920, 19, 64.

stitute the 'soft carbonates'; when cemented by clay or iron compounds, the 'hard carbonates'. The ore is difficult to concentrate, as both the lead and silver (the latter often present as halide in considerable amount) are easily slimed. Removal of silver has sometimes been effected by leaching with thiosulphate solutions and the residues subsequently concentrated for lead.

Mixtures of calcium and lead carbonate are found in the Leadhills district, plumbo-calcite, $d. = 2.7-2.8$, containing 1.2—5.2 p.c. of lead carbonate being of common occurrence. Plumbo-aragonite (0.8—1.3 p.c. lead carbonate) is rare, despite the isomorphism of aragonite and cerussite.¹⁾ This may be accounted for by the comparative rarity of aragonite, relatively to calcite.

Anglesite, $PbSO_4$, derives its name from the island of Anglesey where it was first found at the Parys mines. It is isomorphous with anhydrite, celestine and barytes. It is produced from galena readily when the latter comes into contact with the sulphate solutions generated by the weathering of pyrites. It is rarely found in such quantity as to constitute an ore.

Lead is a constituent of a great many minerals. The sulphide, galena, has its analogues in the selenide, $PbSe$, Clausthalite; and the telluride, $PbTe$, Altaite. The sulphide of lead and tin, $PbS \cdot SnS$, is known as the mineral Teallite. The sulpho-salts of lead are an important group of minerals, many of which like Boulangerite, Bournonite, and Jamesonite are of fairly common occurrence and are characteristic of the cementation zone of ore deposits. In the following list, which is not exhaustive, the names and formulae of some of these are given:

| | |
|-------------------------------------|--------------------------------------|
| $PbS \cdot As_2S_3$ Sartorite | $PbS \cdot Sb_2S_3$ Zinkenite |
| $2 PbS \cdot As_2S_3$ Dufrenoy'site | $2 PbS \cdot Sb_2S_3$ Plumosite |
| $3 PbS \cdot 2 As_2S_3$ Rathite | $3 PbS (Bi, Sb)_2S_3$ Kobellite |
| $4 PbS \cdot As_2S_3$ Jordanite | $4 PbS \cdot Sb_2S_3$ Menegbinitite |
| $5 PbS \cdot 4 As_2S_3$ Liveingite | $5 PbS \cdot 2 Sb_2S_3$ Boulangerite |

¹ N. Collie, *Journ. Chem. Soc.*, 1889, 55, 91.

| | |
|---|---|
| 6 PbS · (Ag, Cu) ₂ S · 2 As ₂ S ₃ Len- gentuchite | 5 PbS · Sb ₂ S ₃ Geocronite |
| 4 PbS · 3 As ₂ S ₃ Baumhauerite | 2 PbS · Cu ₂ S · Sb ₂ S ₃ Bournonite |
| PbS · (Tl, Cu, Ag) ₂ S · 2 As ₂ S ₃ Hutchensonite | 7 PbS · 4 Sb ₂ S ₃ Heteromorphite |
| | 9 PbS · 4 Sb ₂ S ₃ Semseyite |
| | |
| | PbS · Bi ₂ S ₃ Galenobismuthite |
| | 2 PbS · Bi ₂ S ₃ Cosalite |
| | 3 PbS · Bi ₂ S ₃ Lillianite |
| | 5 PbS · 4 Bi ₂ S ₃ Bismutoplagonite |
| | 2 PbS · 3 Bi ₂ S ₃ Chiviatite |
| | 3 (Ag, Pb) S · 2 Bi ₂ S ₃ Schirmerite |
| | 2 PbS · Cu ₂ S · Bi ₂ S ₃ Aikinite |

Mention may be made of Ultrabasite, a sulphide of silver and lead containing 2.2 p.c. of germanium and possibly allied to Argyrodite.¹⁾

The oxidised ores exhibit great variety. Crocoite, the normal chromate, PbCrO₄ has its analogues in Wulfenite, PbMoO₄, and Stolzite PbWO₄. The minerals of lead isomorphous with apatite are an important group; 3Pb₃(PO₄)₂ · PbCl₂, Pyromorphite (or Linnets), 3Pb₃(AsO₄)₂ · PbCl₂, Mimeteite, and 3Pb₃(VO₄)₂ · PbCl₂, Vanadinite. Decloizite, Pb₂V₂O₇, is of interest as a derivative of pyrovanadic acid, and related to this is Pyrobelonite which contains 24 p.c. MnO.²⁾ Mottramite, a mineral found at Alderley Edge, Cheshire and used by Roscoe as a source of vanadium is a basic vanadate of lead and copper, (Pb, Cu)₃(VO₄)₂ · 2(Pb, Cu)(OH)₂. Several natural silicates of lead are known, e.g.: Ganomalite, and Alamosite, the metasilicate PbO · SiO₂, corresponding to Wollastonite;³⁾ Barysilit,⁴⁾ 3PbO · 2SiO₂ and Margarosanite,⁵⁾ PbO · 2CaO · 3SiO₂.

The natural basic salts of lead are of particular interest, in that they are generally crystalline and well characterised, differing thereby from most of the basic salts prepared under

1 Rosicky & Sterbo-Böhm, *Zeitschr. Krys. Min.*, 1920, **55**, 430.

2 Flink, *Geol. För. Förh.*, 1919, **41**, 433.

3 Palache and Merwin, *Amer. J. Sci.*, 1919, **27**, 399.

4 Flink, *Arkiv. Kemi. Min. Geol.*, 1917, **6**, 1.

5 Flink, *Geol. För. Förh.*, 1917, **39**, 426.

artificial conditions, and their relations to other compounds of lead afford a clue to the chemical reactions which have been involved in their formation. They are particularly abundant in the chloride group.

The normal chloride of lead, PbCl_2 , Cotunnite is rare and found as a volcanic sublimate. Many basic chlorides are known, one of which Laurionite, $\text{PbO} \cdot \text{PbCl}_2 \cdot \text{H}_2\text{O}$, is hydrated and corresponds in composition to Pattinson's White, formerly made as a pigment by precipitating lead chloride solution with milk of lime. The others are anhydrous and crystallise either in the tetragonal or rhombic system, shewing thereby, according to Rimann, the persistence of the dimorphism of lead monoxide. The members of the series are:

| | |
|---|---|
| $\text{PbO} \cdot 2 \text{PbCl}_2$ · Penfieldite | $6 \text{PbO} \cdot 2 \text{PbCl}_2$ · Pseudo-mendipite |
| $2 \text{PbO} \cdot 2 \text{PbCl}_2$ · Matlockite | |
| $4 \text{PbO} \cdot 2 \text{PbCl}_2$ · Mendipite | $13 \text{PbO} \cdot 2 \text{PbCl}_2$ · Lorettoite |
| | $14 \text{PbO} \cdot 2 \text{PbCl}_2$ · Chubutite ¹⁾ |

Phosgenite or Cromfordite is a Chloro-carbonate of lead, $\text{PbCO}_3 \cdot \text{PbCl}_2$, an interesting synthesis of which from lead hydroxide and carbonyl chloride has been effected.²⁾

A basic carbonate is known and constitutes the mineral Hydrocerussite, $2 \text{PbCO}_3 \cdot \text{PbO} \cdot \text{H}_2\text{O}$. The rare mineral, Lanarkite, is a basic sulphate, $\text{PbSO}_4 \cdot \text{PbO}$; Linarite, a basic sulphate of lead and copper, probably of the formula, $\text{PbSO}_4 \cdot \text{CuO} \cdot \text{H}_2\text{O}$; Caledonite is similar, though according to Collie, the analyses do not correspond to a definite formula, and Leadhillite (or Susannite) a basic sulphate and carbonate, $\text{PbSO}_4 \cdot 2 \text{PbCO}_3 \cdot \text{Pb(OH)}_2$.

The presence of lead in radio-active minerals is a point of great importance in connexion with the hypotheses which have been advanced to explain its abnormal atomic weight in these circumstances. Many lead minerals containing the

1 H. Corti, *Anal. Soc. Quim. Argentina*, 1918, **6**, 65. E. Rimann, *ibid.* p. 323.

2 W. A. Hamor & H. E. Gill, *Amer. J. Sci.*, 1919 [IV] **47**, 430.

radio-active elements are known, of which the following may serve as examples:

Curite $\text{PbO} \cdot 5 \text{UO}_3 \cdot 4 \text{H}_2\text{O}$; Dewindtite $4 \text{PbO} \cdot 8 \text{UO}_3 \cdot 3 \text{P}_2\text{O}_5 \cdot 12 \text{H}_2\text{O}$; Pilbarite $\text{PbO} \cdot \text{UO}_3 \cdot \text{ThO}_2 \cdot 2 \text{SiO}_2 \cdot 2 \text{H}_2\text{O}$; Plumboniobite $\text{R}_2'' \text{Cb}_2\text{O}_7 \cdot \text{R}_4''' (\text{Cb}_2\text{O}_7)_3$, in which $\text{R}'' = \text{Pb}, \text{UO}, \text{Fe}, \text{Cu}$; $\text{R}''' = \text{Al}$ and metals of the cerium and yttrium groups.

The genetic relationships of many of these minerals are exhibited in their pseudomorphs and their alteration-products. Pseudomorphs of Galena after Bournonite and Pyrrhomorphite are not uncommon, the first indicating the abstraction of constituents (sulphide of copper and antimony), the second, exchange of acidic radicles (phosphate and chloride for sulphide). Similar examples of exchange are seen in the pseudomorphs of Cerussite after Anglesite and Leadhillite, and of gain of constituents in the pseudomorphs of Anglesite after Galena.

The patina which galena acquires on exposure to air consists of lead sulphate and the formation of this is naturally accentuated when the galena contains pyrites, the weathering of which yields sulphuric acid and solutions of sulphates. In peat, however, galena is converted into carbonate, a thick coating being formed in 50 years.¹⁾ In old mines, small pieces of galena are often completely changed into cerussite, and crystals of this mineral 2 inches long are reported by Westgarth Forster to have been formed in 20 years. Matlockite and Phosgenite have also been observed as alteration-products of galena.

Leadhillite, Anglesite and Cerussite were found by L. J. Spencer²⁾ in the old Roman slags at Priddy, and Lacroix observed that the action of sea-water on the old slags at Laurium had led to the formation of a great suite of secondary lead minerals, e.g. Anglesite, Cerussite, Hydrocerussite, Laurionite, Matlockite, Fiedlerite, Phosgenite and Penfieldite.

1 W. Wallace, *Deposition of Lead Ores in Veins*, 1861.

2 *Geol. Mag.*, 1889, 36, 71.

The prolonged action (66 years) of sea-water on metallic lead was shown by Russell¹⁾ to have produced Galena, Anglesite, Cotunnite and Leadhillite.

These reactions of lead, and the easy oxidation of the metal, lend point to observations concerning the rarity of native lead, and its association at Långban in Sweden with arsenious oxide,²⁾ which, if not the actual reducing agent, may at any rate act as a preservative of the metal already formed.

LOCALITIES IN WHICH LEAD ORES OCCUR

England and Wales. In the north of England, lead ore has been extensively wrought in the lower Carboniferous beds (the Lead Measures of Alston Moor), the chief localities clustering round the head-waters of the South Tyne, Tees and Wear, in the counties of Northumberland, Durham and Cumberland. The famous district of Alston Moor is in the last named county. Much lead has also been raised along the Pennine escarpment, chiefly in the Jew and Tynebottom limestones. The upper part of Weardale is now the largest lead-raising district in Britain and mines have been worked there for eight centuries. The veins are especially rich in fluorspar, of which large quantities are now won, but blende is singularly absent, though found in abundance hard by in Alston Moor. In Yorkshire, the chief localities are Lunedale, Swaledale, Arkendale and Wensleydale; to a less extent ore occurs in the dales of the Nidder, Wharfe and Aire; in some places, as at Grassington, the deposits are rich in the Millstone Grit.

In Derbyshire, the main field extends from Buxton and Castleton on the north to Cromford and Wirksworth on the south, and two smaller areas are the inliers of Mountain Limestone at Crich and Andover. This has long been a celebrated lead-province. The mineral rights, except for the

¹ A. Russell, *Min. Mag.*, 1920, **19**, 64.

² As the mineral Trigonite, $Pb_3MnH(AsO_3)_3$. G. Flink, *Geol. För. Förh.*, 1920, **42**, 436.

Crich field, belong to the Crown and the mineral laws, probably of Saxon origin, are unique.¹⁾ Mill Close in Darley Dale is the only mine which has been worked in recent years.

The lead ores of Flintshire and Denbighshire occur also chiefly in the Mountain Limestone formation, and to a less extent in the overlying Millstone Grit. The Holywell district of Flintshire is the richest and includes the important mines of Halkyn, Talaere and Talargoch. The Minera mine in Denbighshire was for many years one of the most prolific in Britain.

The Lake District mines, worked from the thirteenth century, and largely developed by German miners in the sixteenth, are in the neighbourhood of Keswick (Newlands and Blencathra) and at Greenside, on the flank of Helvellyn. The ore, with quartz gangue, occurs in veins in the Skiddaw Slates, of Ordovician age. Lead has also been won in quantity from Carrock Fell and is there associated with copper, zinc, tungsten, etc.

The mines of the Mendips, Somersetshire, have been worked since the Roman occupation, and have at times assumed great importance. In the reign of Edward IV. 10,000 men were employed. The old slags at Priddy, averaging 12 p. c. of lead, have been reworked in quite recent times. The country-rock is Carboniferous limestone and Dolomitic Conglomerate of Triassic age. This district gives its name to the mineral Mendipite, which was discovered at Churchill.

Lead ore occurs in Triassic beds in Staffordshire, Notts and Leicestershire; also at Alderley Edge in Cheshire, where cerussite is found associated with pyromorphite, vanadinite and mottramite. Though economically unimportant, these deposits possess scientific interest, and their disposition and mode of origin are similar, in many respects, to those of Commern and Missouri.

The Shropshire mines are among the oldest and most productive in England. At Shelve, Stiperstones and Snail-

¹ For an account of these, see *Rara Avis in Terra, or the Com-pleat Miner*, T. Houghton. 1680.

beach, there are evidences of extensive working by the Romans. The Roman Gravels and Snailbeach mines have been particularly productive. The lead-bearing veins are in rocks of Cambrian and Ordovician age, in which are basic igneous intrusions about Shelve. The group of veins running west and east carry barytic caps and are now wrought for barytes.

In the adjoining county of Montgomeryshire, the conditions are similar, except that igneous intrusions are absent. Authentic records of mining in Cardiganshire exist from 1485, and the mines were developed by Thurland and Hochstetter, later by Sir Hugh Middleton and Thomas Bushell, the last of whom in 1637 established a mine at Aberystwyth. The ore is rich in silver, the pig lead carrying 40—80 ozs. per ton. One group of these mines, including Goginan, Cwm Sebon, Daren and Esgair Hir, was known as the Welsh Potosi. The chief centres are about Newton and Machynlleth; at present much more blende than galena is won. Other important localities in Wales are Carmarthen, in Carmarthen-shire, Bettws-y-Coed, in Carnarvonshire, and Towyn, in Merionethshire.

The lead ores of Cornwall and Devonshire occur in the slates (killas) of Ordovician and Silurian age, especially near the fringe of the granite areas; they are rich in silver and often associated with zinc and copper. The chief mines in Cornwall are at Penrose, Penwarty, Trevascus and Garras, and in Devonshire in the neighbourhood of Beer Ferrers, Beer Alston, Combmartin and Tavistock.

Isle of Man. Lead ore occurs at Laxey in the Cambrian slates bordering the north edge of the granite, and at Foxdale, on the south side of the igneous intrusion, some of the veins being worked in the granite itself. The galena is rich in silver and the veins are productive at a depth of 2000 feet. Foxdale is now abandoned, and the Great Laxey mine is mainly a producer of zinc at present.

Scotland. The mines at Strontian in Argyllshire were once of importance, but the chief locality at present is the Leadhills in Lanarkshire and Wanlockhead in Dumfriesshire,

the district, formerly known as God's Treasure House in Scotland, lying on the high land about the heads of the Clyde, Tweed, Annan and Nith. The country-rock is of Ordovician age. The mines have been very productive for over two centuries; silver is low, averaging 9 ozs. per ton of lead.

Ireland. Some ore has been raised in the lower Carboniferous limestones of Tipperary, but the chief localities are Glendalough and Lugenure on the eastern edge of the granite of the Wicklow Hills. The veins are worked both in the granite and the Ordovician rocks in contact with it.

OTHER EUROPEAN COUNTRIES

France. The deposits at Poullaouen and Huelgoët in Finisterre are now of little importance. In the Auvergne, lead ore rich in silver (100 ozs. per ton of lead) is raised about Pongibaud, the deposits occurring in veins cutting granite and gneiss, and contemporary with the Tertiary volcanic rocks.

Belgium was once a large producer of lead ore. The chief deposits are at Bleiberg, near Moresnet, and occur in Carboniferous limestone, especially near its junction with the Coal Measures.

Sweden yields a certain amount of lead ore, particularly rich in silver. It is worked at Sala, north of Stockholm, Löfås in Dalecarlia and Guldmedhyttan in Vestmanland.

Germany. Lead ore is wrought in the Devonian rocks at Holzappel, Ems and Tanzberg (where it was worked by the Romans) in the Rhine provinces, and in the same formation, but with many igneous intrusions, in the rich metalliferous region of the Harz, e.g. at Clausthal, Lautenthal, St. Andreasberg and Rammelsberg. At Bleiberg, near Commern, and Mechernich, near Aix-la-Chapelle in the Eifel, the ore occurs in nodules (*Knoten*) in the Bunter sandstone. The ore-body is 65 feet thick and 130 feet below the surface, and the ore constitutes 2.5 p.c. of the whole

material. The output from this deposit has been considerable, though its importance is now much lessened. The same remark applies to the district of Freiberg in Saxony, where lead ore has been mined for eight centuries. The country rock is gneiss, which is intersected by about 900 mineral veins, some of the older groups of which carry silver-lead ores. In the Erzgebirge, south of Freiberg, lead ore is also wrought, especially at Altenberg and Schneeberg. More than half of the output of lead in Germany comes from Upper Silesia where galena and blende occur in Triassic dolomites; the chief centre is Tarnowitz.

Austria and Hungary. At Bleiberg, Raibl and Villach in Carinthia, galena occurs in Jurassic limestone; it is remarkably free from antimony and copper, and yielded formerly the pure *Jungfernblei*. At Laibach in Carniola, the ore is associated with blende, cinnabar and barytes and is a component of fissure-breccias in Carboniferous beds. Other noted localities are Przibram in Bohemia and Kapnik, in the Schemnitz-Kremnitz district of the Carpathians.

Italy. Lead is mined near Turin, Milan, Brescia and Florence, but the most important source of the metal is Sardinia, where the mines are of the greatest antiquity, their working dating from the times of the Phoenicians and Carthaginians. Montevecchio is one of the most important centres in Europe; others of note are Monteponi, Malfatano and Malacalzetta. The last-named, like many old lead fields, has become an important producer of zinc.

Spain has the largest output of lead among the countries in Europe. Many of the mines are, like those of Sardinia, of great antiquity, and after many vicissitudes they were revived last century, upon the close of the Peninsular wars. About two-thirds of the total produce comes from the province of Murcia, on the south east coast, the main centres in which are Almazarron and Carthagena. Almeria, the neighbouring coast province, west of Murcia, is also an important producer, and Jaen, to the north of Almeria ranks next to Murcia in output. Further north, Ciudad Real and

the mountainous borders of the Sierra Morena have also important deposits of lead, rich in silver.

Greece. The Laurium mines in south-east Attica were actively worked six centuries before the Christian era, but declined in productiveness so much in a few centuries, that Strabo (30 B.C.) describes how the smelters "committed to the furnace the old refuse and scoria, and hence obtained very pure silver, for the former workmen had carried on the process in the furnace unskillfully".

The old slags were again resmelted in 1864 and contained then from 8 to 15 p.c. of lead and 2—9 p.c. of zinc. The veins, carrying the ore, occur in schists and crystalline limestones, invaded by igneous intrusions, and are richest near the contact of the Plaka granite.

Asia. This continent does not figure prominently as a lead-producer, though some ore is raised in Anatolia, Asia Minor, in the Hunan province of Central China and in Upper Burma. In the last-named district, at Bawdwin, blende and galena, rich in silver, occur as a replacement in syenitic tuffs. The old slags have been resmelted and since 1915 ore has been raised in considerable quantity. Lead ore is also mined at Kamioka in Japan.

Africa. A fair amount of ore, which is imported to France, is raised in Algeria and Tunis.

Australia. Some lead ore is raised in Queensland, and there is a fair production in the Northampton district of West Australia, where the ore occurs in a granite area intersected by basic dykes. The lodes yield chiefly copper at the surface and lead in depth, and the silver content is small.

The Broken Hill deposits in New South Wales are among the most important in the world. It is estimated that 27 p.c. of the world's production comes from these mines. Cerargyrite was discovered in 1884 and the town of Broken Hill founded in 1886. The ores are now smelted at Port Pirie on the coast, 282 miles distant.

The country rock consists of gneisses and schists, probably of lower Silurian age, highly contorted and folded and traversed by diorite dykes. The main lode is 20—120 feet wide at the surface, 65 feet wide at the 1100 feet level, and is 1.5 miles long, and there are three smaller lodes. The gossan is rich in manganiferous limonite, containing a fair proportion of silver; the cementation zone is 3 inches to 3 feet thick and very rich in silver (8000 grams per ton), and there are considerable deposits of secondary minerals, like cerussite and anglesite, mixed with silver halides; the primary ore averages zinc, 28 p.c., lead 19 p.c. with 30 ozs. silver and 3 dwts. gold per ton. The chief gangue minerals are garnet and rhodonite, with calcite, quartz and fluorite. Floatation methods of dressing have yielded satisfactory results with the intimate mixtures of blende and galena, which could not be resolved by the older methods.

In Tasmania, lead ore occurs in some quantity in the Zeehan and Dundas districts. The concentrates contain 65 p.c. of lead and 65 ozs. silver per ton.

North America.

Canada. The Slocan district in British Columbia is the chief locality for lead ore in Canada and the ores are smelted at Trail. Ore is also raised at Notre Dame des Anges in Quebec and in the Yukon district near the borders of Alaska.

Mexico is an important lead-mining country, the best deposits of ore occurring in Cretaceous limestones, associated with Tertiary volcanic rocks. At Mapimi, Durango, is the great pipe deposit, 100 feet in diameter and worked to a depth of over 1600 feet; the ore averages lead 18 p.c., silver 0.06 p.c. and carries 6 grams per ton of gold: At Santa Eulalia, Chihuahua, the ore occurs in irregular masses, following roughly the bedding-planes of the limestone (Newbury's Chamber Deposit). Jamesonite is mined at Zimapam, and in the state of San Luis Potosí the ore is largely cerussite and pyromorphite, associated with cerargyrite.

The United States occupy the premier position alike in the mining and smelting of lead. The chief regions in which

the ore occurs are the Upper Mississippi, the Rocky Mountains and the Pacific Coast.

In the Upper Mississippi region the industry is concentrated in three districts, Wisconsin (Iowa and Illinois), South East and South West Missouri. In the Wisconsin district the ores are sedigenetic and occur in Ordovician dolomite, partly as metasomatic replacements of the limestone, and partly in gash veins: there are no igneous rocks associated with them. The crude material is low-grade and is concentrated up to 74 p.c. of lead.

The disseminated ores of south east Missouri furnish one third of the total output of the United States. The ore bodies are from 5 to 100 feet thick, 25 to 500 feet wide and 9000 feet long, and the raw ore (yielding 5 p.c. of concentrates) averages 3—4 p.c. of lead and is concentrated to 67 p.c. Silver is low, averaging about 2 ozs. per ton of concentrates. The ore is galena and occurs in granules and nodules disseminated through the Bonnetterre and Potosi limestones (of Cambrian age); blende is almost absent.

Somewhat similar deposits occur in south west Missouri (Kansas, Arkansas, Oklahoma) and are mined largely around Joplin. Zinc is however common and is at present the chief product; bismuth and arsenic are almost absent, and there is but little antimony, copper or silver, hence the metal is easily refined and yields the soft Missouri lead.

In the Rocky Mountains, Colorado used to be an important lead-mining state, though the output now is little more than that of Britain. The deposits are mainly in limestone, near the contact of porphyrite dykes. Much carbonate ore, rich in silver, was won at Leadville, but the ores now are sulphides. Other important localities are Aspen and Montana; the Alta vein (silver-lead) of Montana is said to have been the most prolific in the world.

On the Pacific Coast, Eureka in Nevada was once a very important centre, but its output is now greatly diminished. Utah raised much carbonate and sulphate, but with increasing depth, sulphide ore now predominates. The famous Horn

Silver Mine, in which the deposits occur as replacements in limestone at the contact with andesites, is still producing, though on a smaller scale than formerly. The oxidised zone is 600 feet deep and anglesite and plumbojarosite are abundant.

Arizona and California are relatively small lead-producing states, but the ore is very rich in silver. The most important state in the Pacific is Idaho (which includes the famous Coeur d'Alene); the deposits are in fissure veins in Algonkian (pre-Cambrian) strata, and the raw ores average 8 p.c. of lead and 5 ozs. of silver, the concentrates 50 p.c. of lead and 30 gs. of silver. Some of the lodes are mined to a depth of 2500 feet.

STATISTICS OF LEAD-PRODUCTION

The lead-production of the world increased from about 30,000 tons in the beginning of the nineteenth century to 900,000 tons at the end of that period and, as in the case of several other common metals, e.g. iron, zinc, copper and tin, doubled itself roughly every twenty years. In the year before the great European war (1913), it reached a total of 1,142,264 metric tons (1 metric ton = 1000 kilos = 2204 lbs. = 0.98 long or ordinary ton). Of this vast quantity no less than 83 p.c. came from the following five countries:—

| | | |
|---------------------|---------|-------------|
| U.S.A. | 396,034 | metric tons |
| Spain | 203,000 | „ „ |
| Germany | 181,000 | „ „ |
| Australia | 116,000 | „ „ |
| Mexico | 55,530 | „ „ |

Owing to internal conditions, the Mexican output was only about half the normal during that year. The United Kingdom produced 48,962 metric tons, 30,000 of which were derived from imported ores. The production, in thousands of metric tons, from other countries was: Belgium, 35; France, 28; Austria, 22; Italy, 21; Greece, 18; Canada, 17.

Smaller amounts, from 1000 to 3000 tons, were produced by Japan, Hungary, Russia, and Sweden.

About 81 p.c. of this output was consumed by four countries, the amounts being ¹⁾

| | | |
|-------------------------|---------|-------------|
| U.S.A. | 401,300 | metric tons |
| Germany | 223,500 | " " |
| Great Britain | 191,400 | " " |
| France | 107,600 | " " |

Great Britain is now largely dependent on foreign sources for the lead which it requires, the chief sources of supply being Spain, Australia, the United States and Mexico, though less than a century ago it was the most important lead-raising country of the world. Output was at a maximum between 1856 and 1870 amounting in the latter year to 73,420 long tons,²⁾ and the average from 1845 to 1870 was over 68,000 tons a year.

In 1913 it had declined to 18,462 tons. The total output of Britain from 500 B.C. to 1883 A.D. (2383 years) was estimated by Hunt,³⁾ on the basis of a yearly average of 3000 tons, to be over 7 million tons of lead.

The following table p. 46 shews the yield of lead for the various parts of the British Islands for the years 1847 and 1917.⁴⁾

These figures illustrate the great decline in production which has taken place in 70 years, especially in Wales, Cornwall and Devon, Yorkshire and Shropshire. Scotland (the Leadhills and Wanlochhead) shews a considerable increase in output, and there was a small amount of ore raised in Anglesey in 1917, where there was none in 1847. It may be mentioned in this connexion that Sir John Pettus enumerates

1 *Iron and Coal Trades Review*, 1914, 89, 202.

2 R. Hunt, *Mem. Geol. Sur.*, 1848, 703.

3 R. Hunt, *British Mining*.

4 The data for 1847 are taken from Hunt's *Mineral Statistics*; these for 1911 from the *Home Office Report on Mines and Quarries*, 1917, Pt. III.

| | 1847 lead in tons | 1917 lead in tons |
|-----------------------|----------------------|----------------------|
| England: | | |
| Northumberland . . | 13 233 | 321 |
| Durham | | 2729 |
| Westmorland | | 531 |
| Cumberland | 5702 | 513 |
| Yorkshire | 5223 | 33 |
| Derbyshire | 4250 | 2484 |
| Shropshire | 2769 | 11 |
| Devon | 1026 | — |
| Cornwall | 7304 | 2 |
| Wales: | | |
| Flint | 8122 | 641 |
| Denbigh | | 7 |
| Cardigan | 3492 | 680 |
| Carmarthen | | 36 |
| Carnavon | | 107 |
| Montgomery | 679 | 66 |
| Merioneth | | — |
| Anglesey | — | 5 |
| Scotland | 822 | 2955 |
| Ireland | 1380 | 3 |
| Isle of Man | 1099 | 126 |
| Total | 55701 | 11250 |

several English counties as producing lead ore (1670) where now there is none raised e.g. Cheshire, Leicester, Staffordshire, Buckingham, Dorset, Gloucester and Worcester.

CHAPTER III

THE CHEMISTRY OF ROASTING AND SMELTING

The materials available to the lead-smelter and the methods and appliances which may be used by him vary within very wide limits. The chief ore at his disposal is galena; cerussite may be abundant on occasion and, more rarely, anglesite may constitute an important source of supply. The smelting charge may be composed of a rich

concentrate of galena, or this may be mixed to a notable extent with other ores of lead, along with sulphides of many other metals, and there may be present, to a greater or less extent, earthy and silicious materials, gangue minerals like quartz, calcite, fluorspar and barytes, and additions of limestone, iron ores, etc. may be made at some stage in the operations. The fuel for heating may come into direct contact with the materials of the charge, or it may be separated so that only the gaseous products are concerned in the reactions; lastly, the air penetrates the reacting substances and plays an important part in the changes which take place.

There is thus the possibility of a multitude of changes, both of a physical and chemical nature. In general, the operations involved in the treatment of sulphide ores consist of roasting at a low temperature, whereby the ore is desulphurised and oxidised compounds produced, and smelting the oxidised compounds at a higher temperature, under such conditions that the metal is liberated. Roasting is thus essentially an oxidising process and smelting one of reduction. These two fundamental operations may be separate in time and place, or in time only, or they may occur almost simultaneously. For the purpose of description, we may regard them as completely independent changes.

Before entering upon the discussion of the main reactions of roasting and smelting, it may be well to summarise briefly some of the simpler effects of heat upon the possible constituents of a charge. The sulphides of the metals melt at varying temperatures, some quite easily, and the effect of a low melting point is important in roasting, since it results in the agglomeration of the material and hinders thereby the access of air. The melting points of the sulphides which may be met with under practical conditions are given in the following table: ¹⁾

1 J. H. L. Vogt, *Die Sulfid-Silikat Schmelzlösungen*, 1917.

| | | |
|------------------------------|-----------------------------|--------------------------|
| As_2S_3 310° | Ag_2S 834° | MnS 1620° |
| As_2S_3 220° | PbS 1114° | ZnS 1650° |
| Sb_2S_3 546° | Cu_2S 1130° | BaS 1600—1700° |
| Bi_2S_3 718° | FeS 1183° | CaS above 1700° |

The melting point of lead sulphide is said to be much lower (930°—40°) when rapidly heated; in any case, it sinters at a comparatively low temperature and so, in ordinary roasting, has to be heated with care. Certain of these sulphides (those of lead, iron and zinc) decrepitate easily, and thus give rise to fine dust.

Of the other important materials of a charge, quicklime has a very high melting point, 2572°, and the silicates of iron and calcium which occur in slags have also high melting points, e.g. $2\text{FeO} \cdot \text{SiO}_2$, 1100°; $\text{FeO} \cdot \text{SiO}_2$, 1500°; $\text{CaO} \cdot \text{SiO}_2$, 1540°;¹⁾ lead silicates, however, are easily melted at about 800°. It may be remarked that in practice, one is concerned rather with the temperature of formation of slags than with their melting points when ready-formed and, also, that many of the temperatures of melting of the pure compounds would never be attained; the sulphides, for example, form easily fusible mixtures, the mattes, and the silicates form similarly the slags, and the melting points of these are depressed in accordance with the usual behaviour of mixtures. Again, an infusible compound like quicklime would react with the acidic oxides in its neighbourhood, long before its melting point was attained.

Polysulphides, when, heated, lose part of their sulphur. Iron pyrites, for example, after heating to 700° C has the composition of a pyrrhotine Fe_9S_7 ; this fuses at 925° and the residue after heating to 1200° corresponds in composition to the simple sulphide FeS .²⁾ Similarly, chalcopyrite $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$, loses one fourth of its sulphur when strongly heated. It may be remembered that cupric sulphide does not exist under metallurgical conditions, for at a moderate temperature it loses sulphur and is changed to the cuprous compound.

¹ G. V. Wilson, *Trans. Soc. Glass Tech.*, 1918, **2**, 177.

² E. D. Peters, *The Principles of Copper Smelting*, 1907.

Polymorphic changes produced at a definite temperature (the temperature of transition) as, for example, quartz to tridymite and cristobalite, or blende to wurtzite, have no particular bearing on furnace-reactions.

Volatilisation is an important factor in metallurgical operations. Some elements, like sulphur, arsenic and zinc, volatilise with great ease; antimony and lead require a somewhat higher temperature, and the oxides of these elements are also readily volatile. Zinc sulphide volatilises in quantity at a temperature of 1500° , and even at 1350° is distinctly volatile.

The volatility of galena is strongly marked and has been observed under a great variety of conditions. It was recorded by Lacroix and Jambonini at the eruption of Vesuvius, April 1906, and sublimates of the mineral have been noticed in lead furnaces and in burning coal mines. H. L. Pattinson¹⁾ found that galena was easily volatilised when heated in a current of steam. Even at 800° , under atmospheric pressure the volatility is pronounced,²⁾ and at 600° in the vacuum of the cathode light, the mineral can be distilled. The vapour pressure is 2 mm of mercury at 850° and 17 mm at 1000° .³⁾ Roberts-Austen found that, when heated to 1357° in an atmosphere of sulphur dioxide, lead sulphide lost 38 p.c. of its weight in 20 minutes; in an atmosphere of nitrogen the loss was a trifle less under the same conditions. Heated to 1434° in nitrogen, the mineral lost 72 p.c. in 20 minutes. Other observers affirm that the volatility is greatest in nitrogen.⁴⁾ Lodin⁵⁾ states that a small quantity of lead sulphide is completely volatilised, without fusing, when heated in nitrogen to 860° , and he adds the interesting observation that the compound does not exhibit volatility when mixed with excess of litharge.

1 *Phil. Mag.*, 1829, **5** (ii), 172. Watson's observations on this point have already been noted.

2 Schenck and Raßbach, *Ber.*, 1907, **40**, 2192.

3 Schenck and Albers, *Zeitschr. Anorg. Chemie*, 1919, **105**, 145.

4 H. C. Jenkins, *Journ. Chem. Soc.*, **189**, 151.

5 *Compt. rend.*, 1895, **120**, 1164.

The volatilisation of silver may occasion considerable loss of the precious metal, especially in roasting processes. It is promoted by looseness of the roasting charge, which allows of easy permeation of air and, also, by the presence of such compounds as cuprous oxide and the magnetic oxide of iron, which promote the decomposition of silver sulphate. On the other hand, when the silver is present as arsenate or antimonate, roasting leads to, but little loss. It would appear that the loss of silver during the roasting of silver-bearing lead ores is to be ascribed to the volatility of an oxide, either Ag_2O or Ag_2O , which is produced either by the decomposition of silver sulphate, or by the direct oxidation of the metal.¹⁾

Some of the simpler changes of dissociation and decomposition which possible components of a charge undergo on heating may now be considered.

Lead carbonate (cerussite) suffers dissociation at a low temperature and the dissociation-pressure of the carbon dioxide becomes equal to one atmosphere at 285° . The relationship between temperature and pressure are exhibited in the following table:

| | | | | | |
|---|-----|------|-----|-----|-----|
| Temperature ($^\circ\text{C}$) . . . | 184 | 210 | 233 | 280 | 285 |
| Dissociation-Pressure (mm-mercury) . . . | 10 | 32.5 | 102 | 548 | 760 |

The reaction ceases to be reversible above 350° , owing either to some such change as polymerisation affecting the lead oxide, or to the oxidation of that compound by carbon dioxide.

Calcium carbonate is also dissociated on heating but at a higher temperature than in the former case, the data being:

| | | | | | | | | | |
|---|-----|-----|------|------|------|------|------|-------|-------|
| Temperature ($^\circ\text{C}$) . . . | 605 | 631 | 671 | 691 | 701 | 727 | 748 | 798 | 894 |
| Dissociation-Pressure (mm-mercury) . . . | 2.3 | 4.0 | 13.5 | 19.0 | 23.0 | 44.0 | 70.0 | 138.0 | 710.0 |

Ferrous carbonate (siderite, chalybite) is decomposed about 400° into ferrous oxide and carbon dioxide; manganese

¹ Plattner, *Die Röstprozesse*, p. 113; Guntz, *Compt. rend.*, 1899, 128, 996; Berthelot, *Ann. de Chim. Phys.*, 1901, [7], 22, 289.

carbonate (manganese spar or rhodochrosite) undergoes a similar change.

The sulphates of the metals, though not as a rule present originally in the charge, are produced by oxidation of sulphides during roasting, and form an important group. In most cases the temperature-interval between their formation and decomposition is small; there is no very definite temperature of decomposition; and in mixtures the stability of one particular component may be greatly enhanced, owing to the fact that the concentration of sulphur trioxide in the gaseous phase in contact is kept high by the free decomposition of the less stable members, and thus reverses in part the reaction of decomposition of the more stable component. Oxides are the usual ultimate products of decomposition, but sometimes intermediate stages of basic sulphates are encountered, and silver sulphate leaves a residue of metallic silver.

It will be obvious that a list of temperatures of decomposition of the sulphates would have little or no meaning, but some idea of the relative stability of these compounds may be obtained from the table below,¹ in which the temperatures given are those, for the changes indicated, at which the pressure of the gaseous products of decomposition is equal to one atmosphere. In other words, the temperature is the highest, in each case, at which the sulphate is stable when in contact with its decomposition products at atmospheric pressure:

| Sulphate | Solid Decomposition product | Temperature (°C) at which the gas pressure = 1 atmos. |
|----------------------------------|----------------------------------|---|
| $\text{Fe}_2(\text{SO}_4)_3$ | Fe_2O_3 | 705 |
| CoSO_4 | CoO | 880 |
| NiSO_4 | NiO | 840 |
| CuSO_4 | $2\text{CuO} \cdot \text{SO}_3$ | 740 |
| $2\text{CuO} \cdot \text{SO}_3$ | CuO | 845 |
| ZnSO_4 | $3\text{ZnO} \cdot 2\text{SO}_3$ | ca. 840 |
| $3\text{ZnO} \cdot 2\text{SO}_3$ | ZnO | 935 |
| MnSO_4 | Mn_2O_3 (?) | 1030 |
| Ag_2SO_4 | Ag | 1085 |

¹ K. Friedrich, *Metallurgie*, 1910, 7, 323.

The decomposition of ferric sulphate plays such an important part in roasting that further information concerning it is desirable. The primary decomposition of the salt is into ferric oxide and sulphur trioxide, and the latter compound immediately suffers dissociation, so that the gaseous phase contains sulphur trioxide, sulphur dioxide and oxygen. The total pressure of these at various temperatures is:

| | | | | | | | | | | | |
|------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Temperature (°C) . . . | 553 | 570 | 592 | 614 | 634 | 650 | 660 | 680 | 690 | 699 | 707 |
| Pressure (mm. mercury) | 23 | 33 | 45 | 70 | 113 | 149 | 182 | 286 | 401 | 560 | 715 |

From these results, coupled with the knowledge concerning the dissociation of sulphur trioxide, the partial pressures of the sulphur trioxide in the system at equilibrium can be calculated, and are found to be¹:

| | | | | | | | |
|--|------|------|------|------|------|-------|-------|
| Temperature (°C) | 580 | 600 | 620 | 640 | 660 | 680 | 700 |
| Partial pressure of SO ₃ (mm) | 24.7 | 36.6 | 50.5 | 70.6 | 93.5 | 135.5 | 233.0 |

These data are combined on the curves (Fig. 1), A representing the partial pressure of sulphur trioxide, B the total gaseous pressure.

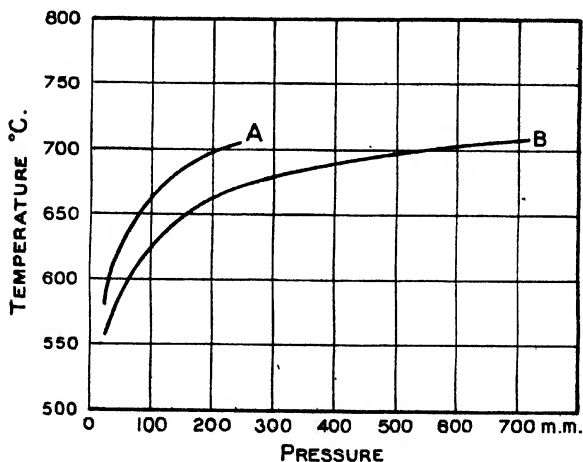


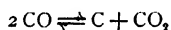
Fig. 1.—Dissociation of Ferric Sulphate.

¹ L. Wöhler, W. Plüddemann, P. Wöhler, *Ber.* 1908, **41**, 703.

Lead sulphate is distinguished by its great stability. It sinters about 950° and begins to lose sulphur trioxide at a slightly higher temperature; its melting point is over 1100° .

The behaviour of the furnace gases at high temperatures calls for some consideration, since all the compound gases undergo dissociation, though in varying degree.

Carbon dioxide becomes appreciably dissociated into carbon monoxide and oxygen above 1100° , but even at 1200° the degree of dissociation is small, not exceeding 0.03 p. c. Water vapour is similarly dissociated into hydrogen and oxygen to a small extent at these temperatures, and methane, a possible product of the decomposition of fuel, is dissociated into carbon and hydrogen.¹⁾ The dissociation of carbon monoxide, as represented by the equilibrium-equation:



is of more importance. Determinations of the volumetric composition of the gases in a state of equilibrium at atmospheric pressure and at various temperatures gave the following values²⁾:

| Temperature ($^{\circ}\text{C}$) | Carbon Monoxide | Carbon Dioxide |
|------------------------------------|-----------------|----------------|
| 850 | 93.7 | 6.3 |
| 900 | 97.8 | 2.2 |
| 950 | 98.7 | 1.3 |
| 1000 | 99.4 | 0.6 |
| 1200 | 99.94 | 0.06 |

The degree of dissociation thus decreases over this range and this is confirmed by Boudouard's estimation at a much lower temperature, 650° , the composition being then 39 p. c. of monoxide and 69 p. c. of dioxide. In the region of 400° , carbon monoxide is completely dissociated; otherwise regarded, carbon is not able to reduce carbon dioxide at that temperature.

The dissociation of sulphur trioxide into sulphur dioxide

¹ H. F. Coward and S. P. Wilson, *Journ. Chem. Soc.*, 1919, **116**, 1380.

² E. L. Rhead and R. V. Wheeler, *Journ. Chem. Soc.*, 1910, **97**, 2174; 1911, **99**, 1140.

and oxygen has been carefully studied in connexion with the contact process for the manufacture of sulphuric acid. In presence of platinum as a catalyst, the composition of the system at equilibrium, at certain temperatures, is as follows:

| Temperature (°C). . . . | | 400 | 500 | 600 | 700 |
|-------------------------|--------------------|-------|-------|-------|-------|
| Volume per cent. | { Sulphur Trioxide | 97.50 | 87.30 | 69.00 | 41.50 |
| | { Sulphur Dioxide | 1.67 | 8.47 | 20.67 | 39.00 |
| | { Oxygen | 0.83 | 4.23 | 10.33 | 19.50 |

Many of the materials present under furnace conditions are efficient catalysts in this reaction. Calcined pyrites (*Abbrand*) comes within this category, and is effective with gases from the roasting of sulphide ores (containing 7 p.c. sulphur dioxide, 10 p.c. oxygen and 83 p.c. nitrogen) between 400° and 850°, giving a 45 p.c. conversion at 550°; quartz has a similar effect.¹⁾

Though there is but little opportunity under furnace conditions, for any of the equilibria described above, to be established, at any rate for a lengthy period, the general nature of the phenomena cannot be overlooked, but must be taken into account in any attempt to study the roasting and smelting reactions in a thorough manner. Where equilibrium is not possible, dissociation will in general lead to results comparable with those of irreversible decomposition. Thus, the dissociation of sulphur trioxide will set up conditions favourable to oxidation by means of oxygen, and the sulphur dioxide set free will either escape or enter into secondary reactions. On the other hand, when bases are in contact with sulphur dioxide and oxygen, the reverse phenomenon of combination, or association, of the two gases will result in their fixation as a sulphate of the base, and the disturbance of equilibrium resulting from the removal of the sulphur trioxide will cause more of the gases to combine, so that, in favourable circumstances, it would not be impossible

¹ R. Knietsch. *Ber.*, 1901, **34**, 4013. Bodenstein and Pohl, *Zeitschr. f. Electrochemie*, 1905, **11**, 385.

for them to be completely absorbed by the base, and retained in the form of sulphate.

The velocity of such gaseous reactions depends in large measure upon the nature of the catalyst or contact substance, and a furnace in working is richly supplied with good catalysts, in the form of heated brickwork, quartz, finely-divided metals, oxides, etc., for all the reactions which have been considered. It should be remembered that catalysts differ from one another in respect only of the velocity of the reactions which they influence. Any acceleration or retardation of this affects both the forward and the reverse reaction in the same manner, so that the composition at equilibrium is unaltered, provided the other conditions remain the same.

Mention may be made of the thermal aspect of this subject. Since the dissociation of most of the gases concerned is accompanied by an absorption of heat-energy, the degree of dissociation will increase with rise of temperature, and the production of heat in processes of combustion, in which these gases are formed, will be less than that calculated by an amount proportional to the degree of dissociation. Carbon monoxide is exceptional in that its production from carbon dioxide and carbon is an endothermal process. Its stability thus increases, according to the well-known principle, with rise of temperature, until above 1200° it is no longer appreciably dissociated. Conversely, when the temperature is lowered, the dissociation becomes manifest by the deposition of soot and the liberation of heat.

THE ROASTING AND SMELTING OF PURE GALENA

THE REACTIONS OF THE AIR REDUCTION PROCESS

Having considered the simpler changes which the various constituents of a charge singly undergo when heated, we may now pass on to the more complex reactions, so fundamental in nature, by which lead is extracted from galena by the agency of air.

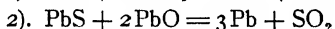
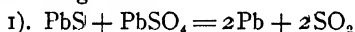
Finely divided lead sulphide, obtained by precipitation, has long been known to be very susceptible of oxidation. Rodwell found that it absorbed oxygen at 50° and gave a smell of sulphur dioxide at 125° . Investigation of galena has shown that it resembles the precipitated sulphide in this respect, as it yields evidence of initial oxidation at so low a temperature as 90° . Friedrich,¹⁾ who established this point, has devoted much labour to the determination of the temperature of ignition of the pure mineral under different conditions. His results are most discordant, but in general the glow indicating ignition varies according to the size of grain and the rate of heating. For grains of .1 to .2 mm. edge, initial glowing is at 847° , when the powder is slowly heated from the ordinary temperature, but at 646° , when the powder is quickly raised to 502° , and it follows immediately when the mineral is put into a furnace heated to 554° . Formation of fume and appreciable liberation of sulphur dioxide were found usually to occur at a slightly lower temperature than glowing. It will be seen later that the ignition of galena depends on the nature of admixed materials and, as a rough estimate, 550° may be taken as the temperature under ordinary furnace-conditions.

The residue from the air-oxidation of galena is a mixture of sulphate and oxide of lead. The formation of the sulphate may be ascribed either to direct oxidation of the sulphide, as suggested by Rammelsberg, or to secondary reaction, resulting from the oxidation of a portion of the sulphur dioxide to sulphur trioxide and the union of this with lead oxide. There is little or no evidence in favour of direct oxidation and, indeed, this would appear to be unlikely on general considerations. It would follow then, on the alternative view, that the composition of the roasted residue will depend upon the conditions of oxidation. Factors which favour the catalytic oxidation of sulphur dioxide, and the contact of the reacting substances, should increase the sul-

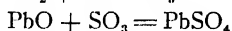
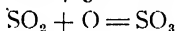
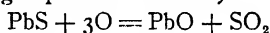
¹ Friedrich, *Metallurgie*, 1909, 6, 169.

phate relatively to the oxide of lead. The practical observation that slow roasting, at a low temperature, favours the formation of lead sulphate is in harmony with this, though there is but little experimental work recorded on this subject. Plattner¹⁾ found that 100 grams of fine galena, *mit aller Vorsicht vollständig abgeröstet*, gained 3 grams in weight, and the product contained 66.3 grams of lead oxide and 36.7 grams of lead sulphate; that is, roughly, twice as much oxide as sulphate was formed. These are the proportions required for the ideal reaction described below.

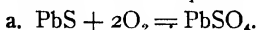
In order to extract lead from galena by the air-reduction process, the roasting of the ore is not carried to completion; at a certain stage the temperature of the partly roasted ore is raised, so that reaction takes place between unaltered lead sulphide and its roasted products. The process is thus frequently, though somewhat loosely, termed "roasting and reaction", and the two fundamental changes involved in the reaction-stage are:



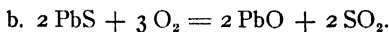
Let us assume that a sample of galena is roasted in such a way that one fifth is converted into sulphate, the changes being represented thus:²⁾



Summation of these equations gives:



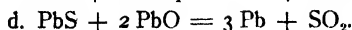
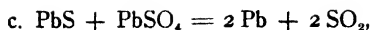
Suppose, further, that two fifths of the galena is oxidised to oxide:



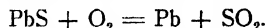
Now, let the remaining galena react with its oxidation-products in accordance with the fundamental equations 1 and 2, then:

1 *Die Röstprozesse*, etc., p. 145.

2 The representation of "molecular" oxygen in such equations is dispensed with as a needless complication.



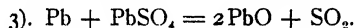
Summing equations a to d, cancelling the terms common to both sides and dividing by five, the result is:



In this simple manner, the chemical significance of the air-reduction process becomes manifest, and the example serves to point the moral, so often overlooked, that a summation-equation may rather mask than make clear the nature of the chemical changes which it professedly explains.¹⁾

The above reactions (1 and 2) are probably the chief concerned in the production of lead from galena, but they are by no means the only ones. The system consisting of lead and its sulphide, sulphate and oxide, and sulphur dioxide, can undergo other changes which may become important under certain practical conditions.

There is no certain evidence that lead reacts with either lead sulphide or lead oxide, but it reduces its sulphate at a fairly high temperature, according to the equation:²⁾

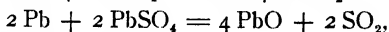
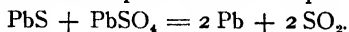


This equation is often combined with No. 1 above, in

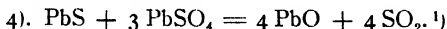
1 Berthier's experiments in this connexion (*Traité des Essais*) are of particular interest in that lead was produced from galena by the aid of such powerful oxidising agents as manganese dioxide and potassium nitrate. The best results are obtained by using a flux. Thus 10 grams of galena added to 30 grams of sodium carbonate gave immediately 7.5 grams of lead on addition of 3 grams of potassium nitrate. Since sodium carbonate and lead sulphate react to form sodium sulphate and litharge, the reaction directly responsible for the metal is probably that between lead sulphide and lead oxide. Armstrong and Hannay (*Proc. Chem. Soc.*, **189**, 113, 151) got a 50 p. c. yield of lead by blowing air through molten galena. The possibility of limiting oxidation in these cases is obvious, and another important factor is the heaviness of molten lead, which ensures its rapid removal from the active oxidising environment.

2 Berthier, *Ann. Chim. Phys.*, 1822, **20**, 275. Also Percy, *Lead*. p. 45.

order to represent the formation of lead oxide in the reaction between lead sulphide and lead sulphate. The two stages are:



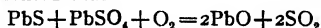
and the sum of these is:



There has been much discussion concerning the temperature at which the principal reactions involved in the air-reduction process take place. Lodin, for example, gives the temperatures of reaction between sulphide and sulphate as 670° (No. 1) and 820° (No. 4), Bannister gives $730\text{--}745^\circ$ for No. 1. For reaction No. 2 (between sulphide and oxide), Lodin gives 720°), Bannister $800\text{--}810^\circ$.³⁾ Though there is agreement as to order of reactions there is considerable difference as to temperatures, and it is obvious that these must depend greatly on conditions. When these are such that the concentration of sulphur dioxide in the gaseous phase is at a minimum, then, since the reactions are reversible, the velocity of the forward reactions will be a maximum. In other words, the temperature of apparent initial reaction, which is that particular temperature at which the velocity of reaction becomes practically measurable, will be lowest, in

1 It is of interest to note that the reaction whereby baryta is produced from barytes in the electric furnace is represented by a similar equation (C. B. Jacobs, *Journ. Soc. Chem. Ind.*, 1902, 391). In both cases the result can be achieved by heating the sulphate to the requisite temperature, which is very high for barytes, with enough carbon to reduce a fourth of it to sulphide.

It may be remarked in this place that many of the equations found in standard books dealing with the metallurgy of lead are compounded of the four fundamental ones described above. Thus the formation of litharge from sulphide and sulphate of lead is sometimes represented thus:



This obviously resolves itself into oxidation of sulphide to sulphate and then reaction between sulphide and sulphate as in No. 4.

2 Lodin *Compt. rend.*, 1895, CXX, 1164.

3 C. O. Bannister, *Trans. Inst. Min. Met.* 1911, 21, 346.

these reversible reactions, when the conditions are such that the reactions become complete, or nearly so. Such conditions, however, may render the observations very difficult.

It is noteworthy that the smelting reactions take place between solid bodies, or preferably when these are in a pasty state. The velocity of the reactions will thus depend largely on the size of the particles, and it is possible, in this connexion, that the volatility of galena is an important factor, since the charge will become permeated with the vapour, or a very fine dust of condensed lead sulphide, as well as of oxide and sulphate formed by oxidation of the vaporous sulphide. In the heap roasting of mattes there is evidence of extensive volatilisation of lead sulphide, and of its oxidation, especially to sulphate; to the same cause is ascribed the fact that the outer shells of roasted lump ore are richer in lead than the kernels.¹⁾

There are several reactions affecting the products of the air-reduction process in which the gaseous constituents take part. The reversibility of the fundamental equations 1 and 2 was indicated by Jenkins and Smith²⁾ in their study of the action of sulphur dioxide on lead, for among the products are found the oxide, sulphide and sulphate of lead. Each equation represents a system of three components in four phases and is thus univariant. The pressure of the gaseous phase, when equilibrium is attained, should therefore be a function of temperature. This deduction from the phase law has been confirmed by Schenck and Rassbach,³⁾ though some doubt has been thrown upon the interpretation of the data by the alleged formation of basic sulphates,⁴⁾ which, if present, increase the number of phases and disturb the equilibrium. Some idea of the pressure at equilibrium of the

1 Plattner, *op. cit.*, 201.

2 H. J. Jenkins and E. A. Smith, *Journ. Chem. Soc.*, 1897, **71**, 666.

3 R. Schenck and W. Raßbach, *Ber.*, 1907, **40**, 2185, 2947; 1908, **41**, 2917.

4 W. Reinders, *Proc. K. Akad. Wetensch.*, 1914, **17**, 703.

sulphur dioxide for the reaction between lead sulphide and lead sulphate (No. 1) may be gained from the following table:

$$\text{PbS} + \text{PbSO}_4 \rightleftharpoons 2 \text{Pb} + 2 \text{SO}_2$$

| Temp. (°C) | Pressure (mm. mercury) |
|------------|------------------------|
| 600 | 39 |
| 635 | 98 |
| 665 | 201 |
| 695 | 402 |
| 713 | 590 |
| 723 | 735 |

The reversibility of this reaction becomes appreciable at 550°, that of the reaction between lead sulphide and lead oxide (No. 2) at 650°, and the latter reaction is characterised by similar gaseous pressures at correspondingly high temperatures. It will be observed that the temperatures at which the reversal of each reaction can be definitely recognised are much lower than those accepted for the direct reactions of smelting (*cf.* p. 59). This is probably to be explained by the difference in physical nature of the reacting materials, which are all solids in the direct reactions, and solid and gaseous in the reverse reactions.

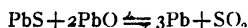
Sulphur dioxide does not react with lead sulphide or lead sulphate, but when lead oxide is heated in the gas to a fairly high temperature, it glows and leaves a residue of lead sulphide and lead sulphate.¹⁾ This result has been confirmed by Hammick,²⁾ who finds the reaction to occur just below visible redness (400—500°). This, therefore, constitutes a reversal of smelting reaction No. 4 and presumably of No. 3 also, since No. 4 is compounded of Nos. 1 and 3 and, again, it may be noted that the recognition of the reversed reaction is possible at a much lower temperature than that of the direct reaction. No attempts appear to have been made to study the phenomena of equilibrium in this case, but the law

1 Plattner, *op. cit.*, 101. The residue is stated to contain also suboxide of lead; this is probably incorrect, but it is likely to contain finely-divided lead.

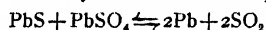
2 D. L. Hammick, *Trans. Chem. Soc.*, 1917, **111**, 379; also, *Uhl. Ber.*, 1890, **23**, 2151.

of phase-equilibrium enables one to infer that they will resemble the other examples, and that the pressure of the sulphur dioxide will be a function of the temperature.

It is thus evident that all the typical smelting reactions of the air-reduction process which take place between lead sulphide and its oxidation products, lead oxide and lead sulphate, as well as the reaction between lead and lead sulphate, by which lead oxide is produced, are reversed by the action of sulphur dioxide on lead and lead oxide. As these reversible reactions are concurrent over considerable intervals of temperature, the relationships are necessarily complex when all phases are present, as must be the case during most of the time in the reverberatory method of treatment. Under favourable conditions of temperature and partial pressure of sulphur dioxide, one of the constituent reactions may remain balanced. To illustrate this consider reaction No. 2:



This is characterised at equilibrium, when the temperature is 755°, by a pressure of sulphur dioxide equal to 38 mm, that is 0.05 atmosphere, and this is the partial pressure of sulphur dioxide when present to the extent of 5 p.c. in an indifferent gas. At the same temperature however, the reaction I. represented by the reversible equation:



requires for equilibrium (according to Schenck and Rassbach) that the sulphur dioxide should exert a pressure of about one atmosphere. This reaction would therefore become complete in the direction from left to right, while the other reaction would remain balanced. The conditions would thus favour the elimination of lead sulphate and, were these the only two reactions in question, might lead to a product eventually containing chiefly lead and lead oxide.

Though our knowledge of these reactions is at present too scanty to enable us to appraise, even approximately, their influence under practical conditions, it must be emphasized, in view of the confusion existing in some standard works on

this subject, that reversal of the smelting reactions must take place, even though there is little opportunity for equilibrium to be established. The desired reactions will thus be delayed in a measure proportional to the extent of the reversal. It is familiar to roasters of galena that roasting is arrested when the partial pressure of the sulphur dioxide attains a certain, comparatively low, value, although the furnace-gases are still rich in oxygen, and this practical observation is readily understood in the light of the facts detailed above. One of the aims of the furnace-man is to arrange for an ample supply of air, and for the removal of the sulphur dioxide. The rabbling of the charge not only exposes fresh surfaces of ore to oxidation, but it liberates also some at least of the imprisoned sulphur dioxide, which in the body of a thick charge can probably acquire a large concentration, and by such means the concentration of sulphur dioxide is kept at a minimum. The reverse reactions are thus diminished, and to an increasing extent when the lead begins to flow, since the metal tends then to remove itself from the sphere of action.

When conditions favour the rapid and continuous removal of sulphur dioxide, the smelting reactions may be rendered quantitative. Thus Lodin¹) confirmed the fundamental reactions 1 and 2 by heating small quantities (about 1 gram) of the requisite amounts of sulphide and oxide, and sulphide and sulphate, of lead, in a stream of nitrogen or carbon dioxide, the proof depending on the estimation of the loss of weight and of the amount of sulphur dioxide liberated. The experimental conditions in this case are such that the concentration of sulphur dioxide in contact with the reacting materials is virtually zero, and they bear little or no resemblance to those encountered in practice.

THE ROASTING OF OTHER SULPHIDES OF THE METALS

Galena is usually accompanied to a greater or less extent by other sulphide minerals, the behaviour of which on roasting must now be considered.

¹ A. Lodin, *Compt. rend.*, 1895, **120**, 1164.

Iron Pyrites is the most easily roasted of all the sulphides. It is also readily decomposed by heat into sulphur and ferrous sulphide. The sulphur distils and is burnt in the state of vapour, the residual ferrous sulphide is then oxidised to ferrous sulphate, provided the temperature be low. At a higher temperature this is decomposed leaving a residue of basic ferric sulphate, or ferric oxide, and evolving sulphur dioxide and sulphur trioxide. Ferrous sulphide, whether present as magnetic pyrites, or in mattes, or formed by the decomposition of complex sulphides like chalcopyrite, shows an analogous behaviour. When there is a deficiency of air some of the iron may be left in the form of the magnetic oxide, Fe_3O_4 .

Copper Sulphide may be present as chalcocite, or in the form of mattes, or it may be derived from chalcopyrite CuFeS_2 . It is oxidised to cuprous and cupric oxides which may then be converted into copper sulphate by the agency of sulphur trioxide. At a higher temperature, the sulphate is decomposed into copper oxide and sulphur trioxide.

Silver Sulphide may occur as argentite or in mattes. When heated in a liberal supply of air at a high temperature, the sulphur is burnt off and metallic silver remains. When mixed with other sulphides, and roasted at a carefully regulated temperature, the silver may be retained in the form of sulphate.

Zinc Sulphide, blende or sphalerite, is the most difficult of all the sulphides to roast, requiring a high temperature and fine division of the particles. The first products of oxidation are zinc oxide and sulphur dioxide, and the former may be converted into zinc sulphate by the sulphur trioxide which is invariably present. At a higher temperature, this is resolved into zinc oxide and sulphur trioxide; basic sulphates are formed at intermediate temperatures.

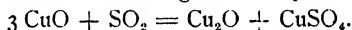
Sulphides of bismuth and manganese yield mixtures of oxides and sulphates, and the latter are decomposed into oxides at a higher temperature, the manganese sulphate with difficulty, the bismuth sulphate easily.

Sulphides of arsenic and antimony on roasting give the volatile oxides, which, being acidic, do not form sulphates, but combine with bases, if these are present, to form arsenates and antimonates.

SECONDARY REACTIONS IN THE ROASTING PROCESS

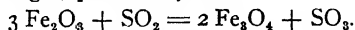
During the roasting of an ore there are present, in general, sulphides, oxides and sulphates of various metals and the gases enveloping these contain sulphur dioxide and sulphur trioxide. There are thus many possibilities of reaction, similar to those described in the case of pure galena. The most important of these are between the metallic oxides and the oxides of sulphur.¹)

The mutual reduction and oxidation of copper oxide and sulphur dioxide was observed by Wöhler and Mahla in 1852 and confirmed by Plattner. Hammick showed that the reaction is quantitative according to the equation:



The reaction is vigorous and sets in below visible redness. As copper sulphate is decomposed at a higher temperature into copper oxide and sulphur trioxide, it should be possible to convert the copper oxide completely into cuprous oxide. The increased absorption of sulphur dioxide at a dull red heat, observed by Hammick, may be an indication of this.

Of the oxides of iron, the triferrous tetroxide, Fe_3O_4 , does not react with sulphur dioxide, but is formed, according to Wöhler and Mahla, from the sesqui-oxide, Fe_2O_3 , by the agency of this gas, presumably thus:



The temperature of reaction is 700–800° (Keppeler). Hammick records that ferrous oxide combines with great ease with sulphur dioxide, yielding a complex product containing sulphur, sulphur trioxide, ferrous sulphide, ferric oxide and both ferrous and ferric sulphates.

¹ See particularly Plattner, *Op. cit.*, 102; Keppeler, *Zeitschr. anorg. Chem.*, 1908, **21**, 579; D. L. Hammick, *Journ. Chem. Soc.*, 1917, **111**, 379.

Zinc oxide decomposes sulphur dioxide at a low red heat, as do many other oxides and furnace materials, into sulphur and sulphur trioxide, without itself suffering much change, though, it is interesting to observe, small quantities of sulphide and sulphate of zinc were detected by Plattner in the residue from this reaction.

The action of sulphur dioxide on the powerful bases of the alkali-earths, especially those containing calcium, is of importance owing to the frequent occurrence of these in roasting charges, either as concomitants of the ores, or as intentional additions. Sulphur dioxide reacts with quicklime at 415° , forming calcium sulphite (the product is either a basic salt, or it is the normal salt mixed with unaltered lime). Absorption of the gas is very rapid at 500° and the product is a mixture of calcium sulphite and calcium sulphate.¹⁾ It is thus apparent that, at the higher temperature, some decomposition of the sulphur dioxide has taken place, and this is confirmed by the observation²⁾ that sulphur and calcium sulphide, as well as calcium sulphate, are produced when slaked lime is used. The influence of moisture on these reactions is very marked, as it is indeed in the union of quicklime and sulphur trioxide. Bannister observed that in roasting galena, the addition of 20 p.c. of quicklime did not suffice to retain all the sulphur dioxide, whereas, with the same amount of slaked lime, the retention of the gas was complete.

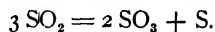
Oxides of strontium and barium are not likely to occur often in roasting-charges; they yield pure sulphites with sulphur dioxide at temperatures between $230-290^{\circ}$. Magnesium oxide absorbs the gas slowly and is converted into sulphate. The behaviour of lead monoxide has already been described (p. 61); there is no certain evidence in this case that a sulphite is formed at any stage in the reaction.

The formation of sulphur trioxide by the catalytic oxidation of sulphur dioxide has already been referred to.

1 K. Birnbaum and C. Wittich, *Ber.*, 1880, **13**, 651.

2 V. H. Velej, *Journ. Chem. Soc.*, 1893, **63**, 821.

There are several other ways in which the compound may be generated under furnace-conditions. The dioxide may suffer direct oxidation, for example, by the agency of copper oxide or ferric oxide, as in the reactions described above. The production of sulphur, sulphide and sulphate of calcium by the action of sulphur dioxide on lime suggests a possible origin of sulphur trioxide (and sulphur) by the decomposition of the dioxide in a manner represented by the equation:

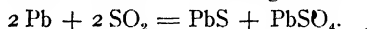


This point has been investigated by Plattner and it is evident that the reaction takes place, with considerable ease in some cases, e.g. in presence of ferrous sulphide (which is readily sublimed in the process). Silica and zinc sulphide also promote the decomposition of sulphur dioxide, though with more difficulty than ferrous sulphide; iron, heated to initial redness, glows strongly in the gas and is converted chiefly into ferrous sulphide, both sulphur and sulphur trioxide being liberated; silver and copper are partly converted into sulphide and sulphate; zinc yields the sulphide, and antimony a mixture of sulphide and oxide.

Observations in this field¹⁾ are neither numerous nor precise, but there can be little doubt that sulphur dioxide does exhibit this decomposition, probably reversible, into sulphur and sulphur trioxide, and that this is a factor in increasing the amount of sulphur trioxide in the furnace gases. Within certain limits of temperature, the gaseous phase will contain not only sulphur dioxide, sulphur and sulphur trioxide, but also some oxygen derived from the dissociation of the trioxide, and many of the reactions, just mentioned, can be explained without difficulty as the result of this initial decomposition of sulphur dioxide, followed by such changes as the sulphur, oxygen and sulphur trioxide can bring about with the solids present, under the conditions of the experiment.

¹ Plattner, *Op. cit.*, 103; Hugo Schiff, *Ann. Chim. Pharm.*, 1861, 67, 94, 95; J. Uhl, *Ber.*, 1890, **23**, 2151.

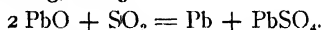
The application of this view to the reactions between sulphur dioxide, lead, and lead monoxide, enables us to gain some insight into the reversal of the smelting reactions, and also to construct the equations by which they are represented. In the case of lead and sulphur dioxide, the temperature may be such that equivalent quantities of sulphur and oxygen are available for reaction with lead, and enough sulphur trioxide is present to neutralise the litharge produced. The summation of the constituent reactions then gives the equation, which represents the reversal of smelting reaction No. 1, viz:



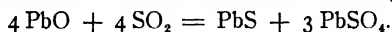
Now, at a higher temperature, the gaseous phase will be richer in oxygen and poorer in sulphur trioxide, owing to the more advanced dissociation of the latter, and the tendency will be for the lead to become oxidised, rather than converted into sulphate. The preponderating constituent reactions in this case will thus be: $3 \text{ SO}_2 = \text{S} + 2 \text{ SO}_3$; $2 \text{ SO}_3 = 2 \text{ SO}_2 + \text{O}_2$; $\text{Pb} + \text{S} = \text{PbS}$; $2 \text{ Pb} + \text{O}_2 = 2 \text{ PbO}$, and their sum is the reversed reaction of smelting No. 2, viz:



In the reaction between lead oxide and sulphur dioxide, the simplest probable change, taking place, presumably, at a relatively low temperature, is that of reduction of litharge to lead, and oxidation of sulphur dioxide to sulphur trioxide; this would then be followed by neutralisation of the basic and acidic oxides. The sum of these yield the reversed reaction of smelting, No. 3:



At a higher temperature, there are superposed on this, effects due to the decomposition of some of the sulphur dioxide; the sulphur liberated combines with the lead formed in the reduction-process, and the rapid fixation of the sulphur trioxide is ensured by the abundance of litharge in the system. The net result is thus the reversed reaction No. 4:



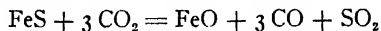
This method of derivation thus gives some account of the genesis of these reactions, based on simple ascertained

changes, and also indicates, qualitatively, variations in reaction, arising from differences in temperature, which are in agreement with observation.

Another important source of sulphur trioxide is the sulphates of the metals, which are formed at a low temperature from the sulphides and decomposed at a higher temperature, usually into oxides and sulphur trioxide.

Sulphur trioxide is a powerful acidic oxide; it is also an oxidising agent, probably by reason of its ready dissociation into sulphur dioxide and free oxygen. These properties give the clue to its reactions in the circumstances under consideration. The basic oxides are converted into sulphates, provided the temperature is below that of decomposition of the sulphates. The metals, lead, silver and copper, as well as their sulphides, are converted into sulphates; zinc sulphide yields a mixture of oxide and sulphate; ferrous sulphide and triferric tetroxide are oxidised to ferric oxide, and even sulphur, carbon and carbon monoxide are oxidised.¹⁾ In all cases where oxidation occurs, the sulphur trioxide is reduced to sulphur dioxide, and as this is again easily oxidised to the trioxide in presence of atmospheric oxygen, the sulphur dioxide plays the part of an oxygen-carrier from the air to the oxidisable constituents of the charge.

Mention may be made here of the fact that carbon dioxide has a slight, but distinct, oxidising action on lead sulphide. When the mineral is heated at 860° in the pure, dry gas, there is continuous evolution of sulphur dioxide and only metallic lead remains²⁾; this is presumably formed by the interaction of lead sulphide and lead oxide. Generally speaking, such oxidation-reactions of carbon dioxide are not observable at temperatures below those at which it is appreciably dissociated. Thus the reaction



cannot be proved to take place below 1150°.³⁾

¹ Plattner, *Op. cit.*, 109.

² A. Lodin, *Compt. rend.*, 1895, **120**, 1164.

³ V. M. Goldsmidt, *Tidskrift Kim.*, 1920, **17**, 215, 221.

Reference has already been made to the action of moisture, which facilitates certain reactions as, for example, the union of lime with sulphur dioxide and sulphur trioxide. There is also a distinct reaction at high temperatures with sulphides of lead, copper, iron and zinc, symbolised by the equation:



In the case of lead sulphide, reaction between oxide and unaltered sulphide takes place, with production of lead and sulphur dioxide, and the latter yields sulphur by its combination with hydrogen sulphide. Thus, the observations of Pattinson, Gauthier and Bischoff are explained, that when galena is heated in steam, there is slight reduction to metal, and the watery distillate is milky from the presence of finely-divided sulphur. Under furnace-conditions, the effect of such reactions must be quite negligible.

THE ROASTING OF GALENA, MIXED WITH OTHER SULPHIDES, GANGUE AND ADDITIONS

Roasting of ordinary ores under reverberatory conditions differs naturally from the roasting of pure galena in many important respects. The various sulphides present have different temperatures of effective roasting; the sulphates which are formed are, in general, readily decomposed and these reactions of decomposition are again dependent on temperature; the sulphur dioxide and sulphur trioxide enter into many secondary reactions, some of which have the effect of reversing the primary reactions desired in the process. Since, for example, the thermal decomposition of many of the common sulphates is reversible, the temperature of effective decomposition will depend on the concentration of sulphur trioxide in the gaseous phase, and in any mixture of sulphates undergoing decomposition, the stability of any one constituent will be in part conditioned by the nature of the other sulphates which are present. It is thus possible to regulate the roasting of a mixture of sulphides, so that one constituent will

be left as sulphate while the others are converted into oxides, as happens in the well-known Ziervogel process of roasting argentiferous copper mattes.

Pyritic ores and mattes are easily roasted; pure galena is slow to roast, and zinc blende increases the difficulty of roasting it. The presence in galena of other sulphides, particularly pyrites, has the effect of increasing the amount of lead sulphate, relatively to lead oxide. In Plattner's experiments on roasting,¹) the results bring out this influence clearly, as seen in the table below, where the ratio of oxide to sulphate of lead is calculated from his data for three cases, namely; (1) pure galena; (3) a mixture of galena and pyrites in equal proportions by weight (these two roasted under laboratory conditions); and (2) slimes from Bleiberg, Carinthia, carefully roasted at a low temperature in a reverberatory furnace.

| | 1. Pure galena | 2. Slimes, containing PbS = 89.5 p. c. ZnS = 7.0 " FeS ₂ = 3.5 " | 3. Galena and Pyrites in equal amounts |
|--|-------------------|---|--|
| Sulphur in the charging material (p. c.). | 13.4 | 16.0 | 33.4 |
| Ratio PbO : PbSO ₄ in the roasted product | 1 : 0.55 | 1 : 1.3 | 1 : 2.1 |

Percy²) supplies the data obtained on the roasting of an ore of the same galena-content as No. 2 in the above example, but containing less sulphur (12.4 p.c.) owing to admixture with carbonates of lead and calcium. The ratio, PbO : PbSO₄, in this case is 8 : 1. The conditions are, however, hardly comparable, since in addition to the ore containing less sulphur, the English method of roasting which was used involves a higher temperature than the Carinthian and the roasting was not complete, since the product still contained

¹ *Op. cit.*, p. 145.

² *Metallurgy of Lead*, p. 235.

64 p.c. of unaltered sulphide. It is probable also that the reaction between lead sulphide and lead sulphate was taking place during the roasting, in preference to that between sulphide and oxide: this would lead to reduction in the amount of sulphate relatively to oxide.

Bannister found that galena mixed with silica, the mixture containing $\text{PbS} = 73.6$, $\text{SiO}_2 = 21.7$ p.c. gave a product, on roasting at 700° , containing still 30 p.c. galena, along with oxide and sulphate of lead in the proportion 1:1.3. The same mixture after roasting at 850° contained 1 p.c. of galena and the proportion of oxide to sulphate was 1:2.3. These experiments are comparable with one another and appear to show that the formation of lead sulphate is favoured by a high temperature, which is contrary to experience on a large scale.

The work of Bannister¹⁾ on the roasting of galena, and the influence of admixture upon the chemical and physical changes which take place, is of considerable interest, though unfortunately marred by the impurity of the galena used in the experiments. The composition of this was: $\text{Pb} = 78.56$, $\text{S} = 11.79$, $\text{SiO}_2 = 2.20$, $\text{Fe} = 2.24$, $\text{Zn} = 1.98$, undetermined 3.23 p.c. It was used alone and also mixed with 20 p.c. of one of the following ingredients: silica, ferric oxide, calcium sulphate, calcium carbonate, magnesia, lead oxide, calcium oxide, calcium hydroxide.

Inactive diluents, like silica and calcium sulphate, facilitate the roasting-process by opening up the ore and allowing of a freer penetration of air. Ferric oxide reduces both the temperature at which roasting begins, and the interval during which it is active, the reduction of temperature being of the order of 100° . Its influence is to increase the proportion of lead sulphate, so that it presumably catalyses strongly the oxidation of sulphur dioxide. As might be expected therefore, its activity depends largely on its physical condition: it appears to be the only 'addition' which acts catalytically. The

1 C. O. Bannister, *Trans. Inst. Min. Met.*, 1911—12, 21, 346.

strongly basic oxides, litharge, magnesia, quicklime, all cause pronounced exothermal reaction, accompanied by glowing, at the temperature of active oxidation of the galena, viz. 500—550°; the reaction with calcium carbonate is similar, but takes place at a temperature about 50° higher. This powerful liberation of heat is evidently caused by combination of the base with the oxides of sulphur. Absorption of these is complete in the case of slaked lime, but the heat of combination is offset by that of decomposition of the slaked lime.

The experiments dealing with the influence of quicklime are more detailed, and of particular interest in view of the frequent addition of this substance to roasting charges. The mixture containing $\text{PbS} = 70.4$, $\text{CaO} = 20.9$ p.c. glowed at 560° and again at 800°. After the first glowing the product contained $\text{PbS} = 28.3$, $\text{PbO} = 28.7$, $\text{PbSO}_4 = 7.3$, $\text{CaO} = 16.0$, $\text{CaSO}_4 = 10.4$ p.c., and after the second glowing, $\text{PbO} = 56.0$, $\text{CaO} = 6.2$, $\text{CaSO}_4 = 29.5$ p.c., lead sulphide and lead sulphate being absent. Thus, after the first glowing, 1.93 p.c. of sulphur trioxide was combined with lead oxide, and 6.12 p.c. with lime. The mean velocity of fixation of sulphur trioxide, in these conditions, is therefore three times as great by lime as by litharge. This would naturally vary with the progress of reaction, falling off as the quantity of lime decreased, owing to conversion into sulphate, and that of litharge increased, but it is evident that lime remains a powerful competitor with litharge for sulphur trioxide, since at the end of the reaction both the litharge and the calcium sulphate have greatly increased and the free lime decreased. The elimination of sulphide and sulphate of lead at this stage must be referred to their reaction, with production either of litharge or of lead; in the latter case the metal has become oxidised directly by atmospheric oxygen.

SINTER- AND SLAG-ROASTING

In the ordinary reverberatory methods of roasting the temperature is kept within such limits that fusion, either partial or complete, of the charge does not take place. For

the subsequent smelting of the ore, when this is performed in the blast furnace, it is necessary that the material should not be powdery, and it is also important that its sulphur content should be low, otherwise the matte-fall will be excessive. If the temperature at the end of the roasting process be raised sufficiently, agglomeration of the charge takes place, or even complete fusion, with the production of a material more suitable, in its physical nature, for feeding into the blast furnace and, at the same time, sulphates are decomposed by reaction with silica, and sulphur, in the form of sulphur trioxide, is expelled. According as the charge is merely fritted or melted down, the process is known as sinter- or slag-roasting.

The sulphates which survive the moderate temperature of ordinary roasting are lead sulphate, calcium sulphate and barium sulphate, and it is these which react with silica at the higher temperature, yielding thereby the fusible silicates of lead, calcium, and barium, and liberating sulphur trioxide. At the same time, the higher oxides of iron may be reduced to ferrous oxide by the agency of ferrous sulphide and the ferrous oxide also combines with silica to form ferrous silicate. The net result is thus further desulphurisation of the charge, and the production of silicates in a form suitable for treatment in the blast furnace.

BLAST ROASTING

This method, in its various modifications, has achieved immense importance since its introduction by Huntington and Heberlein in 1896. The essential feature of all varieties of the process is the rapid passage of air, either by means of blast or suction, through sulphide ore, suitably diluted with materials like lime, limestone, calcium sulphate, oxide of iron and silica. After kindling at one place, oxidation spreads throughout the whole mass, and a product poor in sulphur and in a sintered condition, eminently adapted for smelting in the blast furnace, is obtained. A striking feature of the innovation is the abandonment of the slow and cautious

methods employed in reverberatory practice, for rapid roasting at a much higher temperature.

In the discussion on the chemistry of blast-roasting which followed the wide-spread adoption of the new method,¹⁾ emphasis was rightly laid on the open nature of the charge, owing to the large amount of non-sulphidic material added to the ore, and much attention was directed to the function of lime, limestone and gypsum in facilitating the oxidation process. The latter phase of the problem has now lost much of its old interest, since it is realised that the method can be successfully applied in the absence of these additions. It is essential, however, that the charge should contain not less than 12 p.c. of silica, in order that it may become effectively desulphurised, and the general opinion seems now in favour of the view that the reactions in blast-roasting are similar to those which occur in slag-roasting,²⁾ though of necessity the velocities of the individual reactions are different, since the temperature is higher in the zone of active oxidation, and the access of oxygen and removal of oxides of sulphur are greatly facilitated in that zone.

The importance of the factors last mentioned has been emphasized recently by Rigg,³⁾ who describes them under the title of 'ventilation', meaning thereby that intimate envelopment of ore-particles by air, constantly renewed, which is the main feature of blast-roasting conditions, and is conspicuously absent in the reverberatory process. Stirring the charge in the latter does not effect the dislodgment of much sulphur dioxide, since the stirring apparatus does not work between the grains, and the sulphur dioxide diffuses but slowly, owing to its high density. Some remarkable calculations of this author show that the elimination of sulphur in a day, from one square foot of hearth of the reverberatory type is 5 lbs. but no less than 270 lbs. from one square foot

¹ See the collection of papers in Ingall's *Lead Smelting and Refining*; also Bannister *op. cit.*

² P. Richter, *Min. Ind.*, 1910, XIX, 443.

³ *Bull. Inst. Min. Met.*, 1920, 188, 10.

of a Dwight-Lloyd machine; or, put in another way, the removal of the last 8 units of sulphur from the charge requires 14 hours treatment on the hearth-roasters, and only 14 minutes in the blast roasters.

Where the inflow of air to the incandescent material is greatest, the concentration of the oxides of sulphur is least, and the tendency will be rather for the formation of lead oxide than lead sulphate. There is, however, abundant opportunity for lead sulphate to be formed in the Huntington and Heberlein pots behind the zone of incandescence, especially by the action of sulphur trioxide on lead sulphide. Both oxide and sulphate of lead combine with silica to form lead silicate; they also react with each other, yielding litharge and sulphur dioxide, and this reaction would probably be favoured at the high temperature existing in these conditions. Lead is produced by the fundamental reactions of the air-reduction process, but to what extent it is impossible to say, for metal formed in this way is naturally very liable to oxidation. The problem seems to be rather one of determining the application of well-known reactions to novel conditions, than of seeking explanations in the discovery of new reactions, but until the process has been better studied in its chemical aspects, there must remain much uncertainty as to the course it pursues.

The influence of the calcium compounds on the roasting, referred to above, deserves some consideration, since they are so frequently constituents of the charge. It is generally acknowledged that lime facilitates the roasting of galena. Like all infusible substances, it keeps the particles of galena apart, thereby preventing clotting, and allowing of a better permeation of air. As it combines readily with the oxides of sulphur, it reduces the concentration of these in the atmosphere in contact with the galena, and thus inhibits the reverse reaction by which sulphide of lead is regenerated; and the exothermal nature of its combination with the oxides of sulphur is so pronounced that the temperature of the mass undergoing oxidation is raised considerably, with the result

that the velocity of oxidation is increased. Other functions have been assigned to lime and the other compounds of calcium which have not stood the test of criticism and experiment. Huntington and Heberlein assumed that calcium peroxide acted as intermediary between air and galena, being alternately reduced to quicklime by galena, and reformed from the quicklime by atmospheric oxidation. Though there is nothing fundamentally opposed to this idea, no evidence has been adduced in proof of it. Borchers¹⁾ claimed a similar acceleration of oxidation by the catalytic action of calcium plumbate, and Hutchings by that of calcium sulphate. Others have sought an explanation in reactions between oxides, sulphides and sulphates of lead and calcium. The six possible reactions are between the following pairs:

- 1) Calcium oxide and lead sulphide, or, conversely,
- 2) Calcium sulphide and lead oxide.
- 3) Calcium oxide and lead sulphate, or, conversely,
- 4) Calcium sulphate and lead oxide.
- 5) Calcium sulphide and lead sulphate, or, conversely,
- 6) Calcium sulphate and lead sulphide.

It is generally admitted, chiefly on the authority of Berthier, that calcium oxide and lead sulphide react on strongly heating, and presumably the first products are calcium sulphide and lead oxide. Actually, however, shots of lead and a slag of sulphide and sulphate are obtained (mixed with unaltered lime), from which it would appear that lead oxide had reacted with unchanged lead sulphide, or that lead oxide had been reduced by calcium sulphide, an equivalent quantity of the latter being oxidised to sulphate. This interpretation brings the reaction into complete analogy with that which takes place between lime and cinnabar.

Reactions 3, 4, 5 and 6 have all in turn been asserted and denied by various writers, whence one may conclude that their influence on the roasting process, if they happen at all, will be slight. In this matter, then, we have not advanced

¹ W. Borchers, *Eng. and Min. Journ.*, 1905, **80**, 398.

much beyond the position of Percy, that the action of lime, though "not exclusively mechanical", is nevertheless not distinctly chemical. The results of the many attempts to discover a clue to the numerous reactions which take place, or may possibly take place, in such processes, by the consideration of their thermal effects, can only be regarded as illusory.

THE CHEMICAL REACTIONS OF SMELTING

From the chemical point of view, the simplest method for the extraction of lead from galena is by replacement with another metal. This can be accomplished by heating the galena with iron, copper, antimony, tin or zinc, but iron alone of these furnishes the lead in a pure condition, though the yield is far from quantitative, since some of the lead sulphide passes into the matte and is reduced therefrom with difficulty.

The partial roasting of galena at a low temperature, followed by the heating of the product at a higher temperature, constitutes, as we have seen, a method for the extraction of the metal. Such a process is, however, never complete, for slags rich in lead are obtained which require treatment of a different character, in order that the lead may be recovered. There are also other minerals and technical products, rich in lead, which from their nature are not amenable to the changes characteristic of the air-reduction process. Generally speaking, then, oxidised ores of lead (carbonate and sulphate); metallurgical products like litharge; slags from the air-reduction process, rich in sulphate and silicate; and low-grade, roasted ores containing much gangue, require other methods of treatment, with the end in view of reducing the oxidised compounds of lead to metal, and of fluxing the non-lead materials to form a slag which can be separated more or less completely from the metal.

The most important reducing agents are carbon, in the form of charcoal, coal, coke, peat, by the combustion of which the necessary heat is attained; carbon monoxide derived from it by partial oxidation; and iron, whether added in metallic form or, as is more general, produced from oxide

of iron by the reducing action of carbon and carbon monoxide.

Lead monoxide is reduced by carbon monoxide, even at a temperature of 300° ; ¹⁾ reduction by means of carbon is vigorous at 500 — 600° ; the compound is however fairly stable towards iron. Lead carbonate, of course, behaves like the oxide.

Lead sulphate, like all sulphates, is reduced by carbon to lead sulphide, the carbon being oxidised to carbon dioxide. This reaction takes place at a red heat and is soon followed by secondary changes which set in between sulphide and unaltered sulphate. It is thus possible, in laboratory experiments, by apportioning the sulphate and carbon, and maintaining a favourable temperature, to convert the mixture into either lead sulphide, or lead oxide or metallic lead. ²⁾

Carbon monoxide can also reduce lead sulphate, though at a higher temperature than carbon and, presumably, the same diverse results are attainable; iron reduces the compound to metallic lead.

The reduction of lead sulphate to lead sulphide has an important effect in blast-furnace work, for the ores, no matter how well roasted, contain sulphates and the environment is a reducing one. If the ores contain copper, this is converted completely into cuprous sulphide which, with the sulphides of iron and lead, and other metals, forms those readily-fusible mixtures of sulphides known as the mattes. Study of the binary systems of many of the sulphides shows them to be eutectiferous; thus ferrous sulphide m.p. 1183° and cuprous sulphide m.p. 1130° form a eutectic m.p. 870° ; similarly, ferrous sulphide and lead sulphide m.p. 1114° form a eutectic m.p. 863° , containing 30 p.c. of ferrous sulphide. The ternary and quaternary eutectics of such mixtures probably melt at much lower temperatures. The formation of these easily fusible sulphide-mixtures facilitates the running of the furnace,

1 Brislée, *Journ. Chem. Soc.*, 1908, **93**, 154.

2 P. Berthier, *Ann. Chim. Phys.*, 1822, **20**, 275; Gay Lussac, *Ibid.*, 1836, **63**, 435.

and in addition allows of the recovery of the copper in the charge. The normal composition of lead mattes is:¹⁾ Fe = 45—60; Pb = 10—15; Cu = 5—10; S = 22—25.

Slags from lead furnaces are of two kinds. The grey slags from hearths and reverberatories are often composed largely of sulphates of lead, barium and calcium, and oxide of lead, those from blast furnaces are silicate slags. The former used often to be fluxed completely by the addition of fluorspar. According to Berthier,²⁾ one equivalent of fluorspar and two equivalents either of lead sulphate or calcium sulphate can be melted easily to a limpid liquid; barium sulphate requires twice as much fluorspar to attain the same end. Fusible slags from the smelting of lead ores containing 19 p.c. of barytes at Lea, near Matlock, which required a fluorspar flux in the last stages, were analysed by Berthier and found to contain $\text{BaSO}_4 = 25$; $\text{PbSO}_4 = 22$; $\text{CaSO}_4 = 22$; $\text{CaF}_2 = 16$ p.c.

The silicate slags are self-fluxing, being formed by the union of the basic oxides, or the salts of these with volatile acids, with silica. Though, as we have seen, the formation of lead silicate may be desirable in a roasted ore, it is obvious that a slag from the smelting of lead must be as free as possible from lead, and this is attained by the supply of an ample amount of other powerful bases, like calcium and ferrous oxides, and of suitable reducing agents which can transform either oxide or silicate of lead into the metal. The correct apportioning of the materials of the charge, so that all the earthy and silicious components may unite to form a clean slag of desirable properties is thus a very important matter, to which attention will be given later. For the present, it will suffice to mention the classification of silicate slags and some of the properties of the silicates of lead.

The naming of slags is based on the ratio of acidic to basic oxygen, that is, oxygen united to silicon and to metal

¹ Hofman, *Metallurgy of Lead*, p. 392.

² P. Berthier, *Voyages Métallurgiques en Angleterre*, 1839, Tome II.

respectively, the formulae being represented in analytical manner. In the following table, the composition of slags derived from bi- and ter-valent metals (M'' and M''') are given for the various groups:

| Name | Composition | | |
|-------------------------------------|-------------------------------|------------------------|-----------------------------|
| | Acidic Oxygen Basic Oxygen | M'' = bivalent metal | M''' = trivalent metal |
| Sub-silicate . . | 1 : 1.5 | $3 M''O \cdot SiO_2$ | $M_2'''O_3 \cdot SiO_2$ |
| Singulo- (uni- or mono-) silicate . | 1 : 1 | $2 M''O \cdot SiO_2$ | $2 M_2'''O_3 \cdot 3 SiO_2$ |
| Sesqui-silicate . | 1.5 : 1 | $4 M''O \cdot 3 SiO_2$ | $3 M_2'''O_3 \cdot 9 SiO_2$ |
| Bi-silicate . . . | 2 : 1 | $M''O \cdot SiO_2$ | $M_2'''O_3 \cdot 3 SiO_2$ |
| Tri-silicate . . . | 3 : 1 | $2 M''O \cdot 3 SiO_2$ | $2 M_2'''O_3 \cdot 9 SiO_2$ |

For the bi-valent metals, the singulo-slugs correspond to the orthosilicates and the bi-slugs to the metasilicates. The actual weights of the basic oxides required to form a particular silicate vary according to the equivalent weight of the base. Thus in the following table of Peters¹⁾ are given the data for some simple bi-silicates, and the calculation of the replacement-value of the basic oxides concerned:

| Bi-silicates | Basic Oxide | Acidic Oxide | Basic Oxide Acidic Oxide | Replacement Value of Basic Oxide |
|-------------------------|-------------|--------------|-----------------------------|--|
| | p. c. | p. c. | | |
| $MgO \cdot SiO_2$. . . | 40.0 | 60.0 | 0.66 | 1 |
| $CaO \cdot SiO_2$. . . | 48.3 | 51.7 | 0.93 | 1.4 |
| $FeO \cdot SiO_2$. . . | 54.5 | 45.5 | 1.20 | 1.8 |
| $PbO \cdot SiO_2$. . . | 78.8 | 21.2 | 3.7 | 5.5 |

In lead smelting by the blast-furnace process, the object aimed at is to produce a monosilicate slag, mobile when molten, and having a sp.gr. of 3.5. Analyses of slags of proved merit are given in the following table:

| | (Fe, Mn)O. | (Ca, Mg)O. | SiO_2 |
|----|------------|------------|---------|
| 1. | 50 | 12 | 28 |
| 2. | 40 | 20 | 30 |
| 3. | 33 | 24 | 33 |

1 Principles of Copper Smelting.

Smythe's Chemistry of Lead

No. 1 is the Freiberg type, and is especially valuable for charges rich in zinc, which makes the slags viscous and raises their temperature of formation: such slags should be highly ferruginous and correspondingly poor in silica, and the amount of zinc (reckoned as oxide) should not exceed 15 p.c. According to Hutchings,¹) zinc is present in slags as the silicate (willemite), zinciferous magnetite and zinc spinels. This has been confirmed by Rigg²) in his study of slags, rich in zinc, at Port Pirie. The analysis of the slag showed $\text{ZnO} = 31.8$, $\text{FeO} = 20.3$, $\text{MnO} = 4.9$, $\text{CaO} = 9.0$, $\text{SiO}_2 = 18.3$ p.c. This does not conform in composition to any of the standard types, and yet its properties, in actual working conditions, were quite satisfactory. It would appear that high zinc-content of slags is only objectionable in presence of sulphur. The problem of recovering zinc from such rich slags is one which will have to be considered in the near future.

Iron slags are more fusible than calcium slags and thus lead to less volatilisation of metal. Manganese acts like iron, but raises slightly the temperature of formation. Cases are on record in which furnaces have run successfully while producing highly manganiferous slags (up to 43 p.c. MnO) of type 1 above. Baryta is a good flux for silica, but the sp.gr. of the slags produced is high, and the effect of barium sulphide (derived from barytes) is altogether bad. Alumina thickens slags without raising greatly their temperature of formation, while magnesia has both effects and its presence has to be corrected by iron. Fluorspar has a slightly favourable effect on blast furnace slags.

There is a limit set to the temperature attained in smelting by the fusibility of the slag. In lead-smelting, a low-temperature is sought, and hence the composition of the charge must be arranged to yield a low-melting slag. The temperature of formation of a slag is higher than the melting

¹ *Eng. and Min. Journ.*, Oct. 1903.

² G. Rigg, *Bull. Inst. Min. Met.*, 1920, **188**, 1.

point of the ready-formed slag; much depends, as might be expected, on the size of the component particles; when these are small, then the temperature of formation approximates to the melting (or softening) point of the slags, but with lump material the difference may be considerable.¹⁾

Statements concerning the silicates of lead are somewhat discordant, but it is probable that three can be produced under laboratory conditions, namely, the orthosilicate $2\text{PbO} \cdot \text{SiO}_2$ m.p. 746° ; the metasilicate $\text{PbO} \cdot \text{SiO}_2$ m.p. 766° , corresponding to the minerals ganomalite and alamosite, and a third of the composition of barysilite $3\text{PbO} \cdot 2\text{SiO}_2$.²⁾ The melting points of these silicates are lower than those of litharge and silica. The silicates produced in practice are probably indefinite mixtures of these, which hold litharge or silica in solution, according to their degree of basicity or acidity. They are easily fusible, even when silica is present in large excess. Those rich in lead are partly reducible by means of carbon and even by ferrous and lead sulphides. All of them can be reduced by iron, lead being replaced and ferrous silicates formed. Ordinarily, during smelting operations, they are heated with powerful bases—lime, ferrous oxide, manganous oxide, etc.—in presence of reducing agents; redistribution of oxides takes place and the litharge, as soon as it is replaced from combination with silica by the other basic oxides, is reduced to lead, and thus removed from the reacting system.

THE METHODS USED IN SMELTING GALENA

These may be classified according either to the chemical changes involved, or to the nature of the appliances used. The chemical methods are: 1. reduction by means of metallic iron, usually known as the precipitation- or iron reduction-process; 2. partial roasting in air followed by strongly heating of the roasted mass; this is the air-reduction or the roasting

1 T. Turner, *Journ. Soc. Chem. Ind.*, 1905, **24**, 1142.

2 S. Hilpert und P. Weiller, *Ber.*, 1909, **42**, 2969; 1910, **43**, 2565; H. C. Cooper, L. J. Shaw and N. E. Loomis, *Ber.*, 1909, **42**, 3991.

and reaction process; 3. roasting of the ore followed by reduction with carbon, or the roasting and carbon-reduction process.

These operations may be carried out in reverberatory furnaces, in which the material is separated from the fuel and the air supply is provided by natural draught, or in shaft furnaces of various types, in which the fuel is mixed with the ore, and air under pressure is blown through the charge. None of the three chemical methods is alone adequate for the extraction of all the metal in any technical operation. For the iron-reduction process in its original form, this was approximately the case, but the process is now extinct. The reaction, however, probably occurs to a slight extent in blast-furnace practice, though in this case the reducing action of iron finds its greatest application in replacing lead from its silicates, and not from its sulphide.

The typical method of using the air-reduction reactions is in the reverberatory furnace, but even here the result lacks completeness, since there are residues rich in lead which require further treatment, involving other reactions, usually in a shaft furnace. When the ore-hearth is used to smelt galena, the air-reduction reactions undoubtedly play an important part, but the intimate contact of ore and fuel necessarily carries with it the possibility of considerable reduction of oxide by means of carbon. Here, again, there are rich slags which demand different treatment.

Smelting in shaft furnaces necessitates the previous roasting of the ore, for the atmosphere is a reducing one. Fuel and fluxes are mixed with the roasted ore and the fluxes include a large proportion of easily reducible compounds of iron. The conditions and materials are such, that all the reactions described above can take place, though possibly reduction of oxide of lead by carbon, and of silicate of lead by iron, are the main ones concerned in the liberation of the metal.

For descriptive purposes, the classification of methods according to the furnaces employed is to be preferred to that

depending on the chemical reactions. The choice of a particular method in practice depends on many factors, which will receive consideration in connexion with the description of the processes.

CHAPTER IV

EXTRACTION OF LEAD IN THE REVERBERATORY FURNACE AND ORE HEARTH

EXTRACTION OF LEAD IN THE REVERBERATORY FURNACE

The simplest practical method of extracting lead from galena is, chemically speaking, that in which the reverberatory furnace is employed, for the ore-concentrate is, necessarily, of a high degree of purity; it is unmixed with other materials during the greater part of the time it is under treatment; it does not come in contact with the fuel, but only with the hot gases from the grate; and the suite of chemical changes whereby the greater part of the lead is liberated can be carried out in the same furnace, without it being necessary to do more than to stir the charge, and to regulate the temperature and access of air.

The chemical reactions involved in the process are those of air-reduction, that is the ore is partly roasted and then, when the oxidation is deemed to be sufficiently advanced, the resulting mixture of sulphide, sulphate and oxide of lead is more strongly heated, in order to bring about the well-known reactions which result in the formation of lead and sulphur dioxide. There are thus two characteristic stages in the operations, those of roasting and of smelting. These are fairly distinct in point of time, though obviously it is impossible to control the temperature and the composition of the enveloping atmosphere so precisely that overlapping does not take place. The period during which smelting is predominant is frequently, though somewhat inaccurately, termed the period of reactions.

The simplicity of the ideal process is not attained in

practice, and for several reasons. The fundamental reactions of roasting and smelting, even in the case of pure galena, are restricted by reversible reactions among the products, and the presence of other sulphides and gangue-minerals introduces secondary changes, some of which are detrimental to the end pursued. Under practical conditions, the chief result of these is to delay the process, and to effect alterations in the composition of the products. There are, however, other factors which militate against the simplicity of the operation, and one of the most important is, the inability of the smelter to control adequately the composition of the charge, so that the ideal reactions become only approximately realised. The result is that roasting and smelting must be repeated, and there is left eventually a residue, no longer amenable to air-reduction from its very composition. Addition of a reducing agent to this may effect a partial separation of the lead it contains, but in any case there is a residue, rich in lead, which must be subjected to special treatment in order that the metal may be recovered.

Variations in the method adopted arise from several causes. The nature and proportion of the ore-associates naturally demands, in some cases, a particular method of treatment; it may be preferred to draw the residual slags from the furnace in a solid (or pasty) condition, or to melt them down, possibly after addition of a flux, and tap them in the molten state: it may be more economical to use the reverberatory to extract a portion of the lead in the ores quickly, and as pure as possible, leaving the remainder for recovery in another way, or to get the maximum yield of the metal, thus leaving a small proportion of residues for subsequent treatment. Again, the size of the furnaces and of the charges smelted in them, and the temperature at which the reactions are performed, may vary within considerable limits, and such variations constitute in the main the basis of a classification. In the English method, large charges are worked quickly at a high temperature; in the Silesian, large charges are treated at a low temperature, and in the

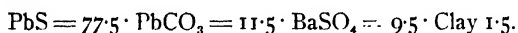
Carinthian method, the furnaces and charges are small and the temperature low.

One result of these variations is that the extent to which the fundamental reactions of roasting and smelting occur varies considerably. On this point our knowledge is very deficient, as is apparent from the discordant statements encountered in the literature of the subject, and in consequence of the totally inadequate analytical data extant. In general it may be stated that slow roasting at a low temperature favours the oxidation of galena to lead sulphate, whereas the formation of lead oxide is favoured by rapid roasting at a high temperature; and of the smelting reactions, the order of greatest velocity, as the temperature is raised, is, lead sulphide and lead sulphate; lead sulphide and lead oxide (lead and sulphur dioxide being the products in each case); and lead sulphide and lead sulphate, reacting to form lead oxide and sulphur dioxide. We are totally ignorant of the manner in which various mixtures of all three reactants behave, with respect to the participation of each fundamental reaction, at different temperatures. Two points of great practical importance are that the temperature of roasting should never be so high that the ore becomes agglomerated, and the smelting reactions are most effective when the material is in a sticky condition.

Ores suitable for treatment by the reverberatory method should contain over 60 p.c. of lead; usually they are much richer, with 70 p.c. or more of lead. Admixture with carbonate is an advantage as the roasting period is shortened thereby, and a limited proportion of lead sulphate is allowable. Pyrites or blende, in small quantity, is not harmful, and indeed the former is beneficial in roasting, and carbonates of calcium, magnesium and iron in moderate amount tend to keep the charge stiff and prevent premature melting. Arsenic and antimony are obnoxious, even in small quantity, and silica must not exceed 5 p.c., otherwise the formation of lead silicate hinders the reactions. Some analyses of ores are given herewith:

| | Composition of Ores | | | |
|--|----------------------|--------------------|------------------------|--------------------------|
| | Raibl (Carinthia) | Engis (Belgium) | Tarnowitz (Silesia) | Holywell (Flintshire) |
| PbS | 76.6 | 93.6 | 61 | 89.9 |
| PbCO ₃ . . . | 4.0 | — | 24 | 6.1 |
| PbSO ₄ . . . | — | — | 11 | — |
| ZnS | 13.2 | 3.7 | — | 1.0 |
| FeS ₂ | — | 2.3 | — | 0.4 |
| Sb ₂ S ₃ | 0.2 | — | — | — |
| CaCO ₃ . . . | 4.6 | 0.3 | 3 | 1.1 |
| SiO ₂ | 0.4 | — | 1 ¹ | 0.8 |
| | 99.0 | 99.9 | 100 | 99.3 |

As an extreme, the analysis of a highly barytic ore which used to be smelted near Matlock, Derbyshire, may be quoted:—



The products of smelting are lead, flue dust, and the residual slags known as grey slags. The composition of these slags is shown in the following table; it may be noted, that the silica in the slags occurs as lead silicate, and though it is conventional to represent this as PbSiO₃, we have no means of determining what amount of lead oxide is equivalent to the given amounts of silica.

| | Composition of Slags | | |
|--|----------------------|----------|-------------------------|
| | Engis (Belgium) | Missouri | Bagillt (Flintshire) |
| PbO | 35.4 | 34.9 | 38.1 |
| PbS | — | 20.9 | — |
| PbSO ₄ | — | 2.3 | 18.7 |
| ZnO | 20.8 | 7.1 | 12.0 |
| (Al, Fe) ₂ O ₃ . . . | 14.7 | 3.8 | 4.6 |
| (Ca, Mg)O | 3.7 | 8.5 | 13.5 |
| S | 0.1 | — | — |
| SiO ₂ | 25.4 | 21.4 | 12.3 |
| | 100.1 | 98.9 | 99.2 |

The general conduct of operations may be briefly sketched. The ore to be smelted must be small. It may consist of slimes, or of lump ore broken to pass through a 4 or 5 mesh sieve. It is spread over the hearth to a depth of about 3 inches. Roasting begins at a visible red-heat ($500-600^{\circ}$) and lasts for several hours, the fire being kept low and the grate open, and the ore being frequently stirred to expose fresh material. At the end of this period, the fire box is filled up and the temperature of the furnace raised to about 800° : the reactions of smelting then take place. When the lead ceases to flow, lime is added to the charge in order to stiffen it and the roasting and reduction processes are repeated. Towards the end of the operations, a little slack coal is added to bring about reduction of lead oxide to metal, and of lead sulphate to lead sulphide, and the regeneration of the sulphide makes possible the elimination of a further amount of oxide and sulphate. Each successive operation reduces the weight of the charge, and consequently takes less time for its completion, and the temperature rises progressively owing to the stiffening of the slags with lime.

The complete chemical study of this process has been made, in one particular instance, by Percy¹) and the data, slightly amplified by additional calculations, are given in the table below. The operations were conducted in the Flintshire furnace at Holywell, the ore had the composition given on p. 88 namely: $\text{PbS} = 89.9$, $\text{PbCO}_3 = 6.1$, $\text{ZnS} = 1.0$, $\text{FeS}_2 = 0.4$, $\text{CaCO}_3 = 1.1$, $\text{SiO}_2 = 0.8$ p.c. and contained 82.7 p.c. of lead and 12.4 p.c. of sulphur; the original charge weighed 21 cwts. and its approximate weight at different stages is taken from Collins²) and given in the last line in the table on p. 90.

The oxides of zinc, aluminium and iron (not given separately in the table above) all increase regularly as the charge decreases in quantity, and their sum, as given above, shows this relationship well, since e.g. $2.13:13.39 = 1:6.3$ is

1 *Metallurgy of Lead*, p. 235.

2 Collins, *Metallurgy of Lead*, p. 35.

| | Composition of the Charge at Various Stages | | | | |
|---|---|--|--|--|-----------------|
| | I. After roast- ing (1½ hours) | II. After roast- ing and melt- ing down (3½ hours) | III. After sett- ing up with lime (4¼ hours) | IV. After setting up with lime and roasting (4¾ hours) | V. Grey Slag |
| PbS | 63.82 | 53.32 | 24.76 | 4.35 | 0.90 |
| PbO | 30.04 | 35.01 | 48.23 | 57.82 | 56.12 |
| SO ₂ | 1.00 | 1.26 | 1.83 | 3.70 | 2.60 |
| CaO | 1.32 | 2.14 | 7.38 | 11.51 | 12.68 |
| SiO ₂ (as silicate) ZnO, Al ₂ O ₃ , Fe ₂ O ₃ (soluble in acid) | — 2.13 | — 4.54 | 8.32 7.97 | 11.04 9.97 | 12.52 13.39 |
| SiO ₂ , Fe ₂ O ₃ , Al ₂ O ₃ , CaO (insoluble in acid) . . . | 1.60 | 3.99 | 1.12 | 0.80 | 1.45 |
| Totals . . . | 99.91 | 100.26 | 99.61 | 99.19 | 99.65 |
| Sulphur (as Sul- phide) | 8.57 | 7.16 | 3.32 | 0.58 | 0.12 |
| Lead | 81.36 | 78.66 | 66.22 | 47.86 | 52.88 |
| Weight of charge | 18 cwts. | 8 cwts. | 4 cwts. | 3.5 cwts. | 2.75 cwts. |

practically the same proportion as that of the charges $2.75:18=1:6.5$. These are the "fixed and invariable" constituents of Percy, and the quantitative relation between them and the total lead in the charge indicates, as Percy points out, that reduction occurs even during the roasting process. The large increase of lime at stage III is due to its addition during the setting up of the slags. There is nothing in the analytical data to show how this is combined; but as, at stages III., IV. and V., it is largely in excess of the sulphur trioxide (the lime equivalents of which are respectively 1.28, 2.59, 1.82), and as it is very probable that the combined silica is present to a considerable extent as lead silicate, which would imply that there was not much free lead oxide present, since the lead oxide equivalents of the silica (for a metasilicate) are 30.9, 41.1 and 46.5, it seems legitimate to draw the following conclusions:—first, that

after the first setting up with lime the charge contains sulphate of calcium only, not sulphate of lead; this would be in agreement with Bannister's observations (p. 72); secondly, as there is a large decrease in the amount of lead sulphide from III to IV, accompanied by increase of calcium sulphate from 3.1 to 6.3 p.c. and a small increase in the weight of the charge, it would appear that the lead produced in this stage has been by reaction between lead sulphide and lead oxide, the presence of the lime preventing the formation of lead sulphate; thirdly, since the calcium sulphate decreases from 6.3 in IV. to 4.4 in V. and the remaining lime shows a corresponding increase from 8.9 to 10.8 it is probable that lime enters into active competition with lead oxide for silica, and that the grey slags contain some calcium silicate, part of which has been derived from calcium sulphate, with corresponding loss of sulphur trioxide.

Percy noted as remarkable the co-existence of such a large proportion of sulphide and oxidised compounds of lead in the product at stage II, and offered a possible explanation based on the "solution or absorption" of sulphide of lead by the metal, the sulphide securing, thereby, protection from oxidation. Equally striking is the small amount of lead sulphate at this stage, for the 2 p.c. of lime is more than enough to combine with 1.26 p.c. of sulphur trioxide, its equivalent of sulphur trioxide being in fact 3 p.c. This may mean that sulphate of lead reacts preferentially to oxide of lead with unaltered galena at the comparatively low temperature subsisting at this stage of the process, and would be in harmony with laboratory experiments, already described, on this subject. On the other hand, assuming all the sulphur trioxide in product I to be present as lead sulphate, the ratio of lead oxide to lead sulphate then becomes 27.2: 3.8 or about 8: 1. This is very different, indeed, from Plattner's result on the complete roasting of pure galena under laboratory conditions, where the ratio obtained was about 2: 1; or again, from the roasting of slimes of the same galena-content though containing more blende and pyrites, and therefore more

sulphur (16 p.c.) by the Carinthian process, for which case Plattner's analysis gives the ratio 1:1.3. The occurrence of lead sulphide (0.9 p.c.) in the grey slag is unexpected since, apparently, coal was not added to the charge for the purpose of reduction. It is possibly accounted for by the incomplete oxidation of the largest fragments of galena which, becoming enveloped in slag, are preserved from reaction, even though probably melted in the final stages.

The study of Percy's data thus raises more difficulties than it explains, and it is evident that much more detailed chemical information on the subject is necessary before we can speak with confidence concerning even the chief reactions operative during the air-reduction process, as carried out in the reverberatory furnace. The alleged chemical objects of the variations of the process, described by writers on the subject, are thus quite beside the point, as might indeed be inferred from the contradictory nature of their statements.

Some practical details relating to the chief methods of reverberatory smelting will now be considered. The recognised varieties of the process are English, Silesian and Carinthian; to these may be added the now extinct French (Breton or Brittany) process, and the closely-related Cornish method, which possess considerable interest both from the chemical and the technical point of view.

THE ENGLISH METHOD

The chief characteristics of this method are the employment of large furnaces and charges, and the rapid roasting of the ore at a high temperature. The yield of lead is high and there is, naturally, a rather high loss of lead by volatilisation. The reverberatory is known as the *Flintshire Furnace* and the modification of the original used at Couëron, Loire Inférieure, France, is illustrated in the accompanying diagrams. Of these Fig. 2. is a longitudinal section, Fig. 3. the horizontal section on the line *CD* of Fig. 2., and Fig. 4. the transverse section through the tapping hole.

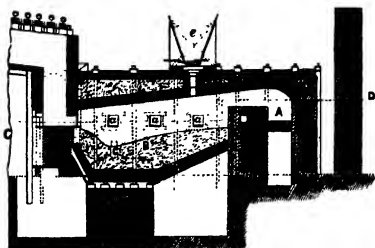


Fig. 2.—Flintshire Furnace: Longitudinal Section.

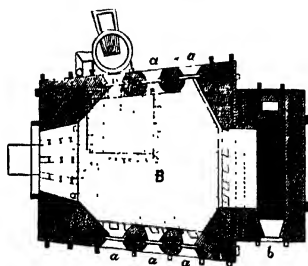


Fig. 3.—Flintshire Furnace: Horizontal Section.

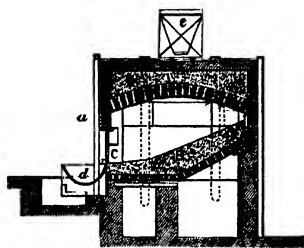


Fig. 4.—Flintshire Furnace: Transverse Section through the tapping-hole

The fireplace is shown at *A* the fire-door at *b*. The hearth, *B*, is trapezoidal in shape, about 11 feet long and 9 feet wide in the mean, with an area of about 100 square feet. It is supported on iron bars on which is laid a course of flat

tiles, and over this a course of fire-bricks standing on end. The actual working-bottom is made of grey slags, moulded into shape when hot and somewhat plastic and from 6 to 12 inches thick. The whole is open beneath, not resting, as in the Flintshire furnace proper, on an air-vault. The six working doors are shown at *a*, the tapping hole at *c*; and the lead pot *d*, below which is a small fire-place by means of which the lead can be kept hot during ladling, is placed in front of the third front door. This arrangement, coupled with the unsymmetrical position of the fire-place and flue, allows of the lead being collected in the coolest part of the furnace, and makes available a large area of hearth for roasting purposes. The ores are charged through the hopper *e*.

The method of working is as follows. A charge of 27 cwts. is let down into the furnace, hot from a previous operation, and spread out over the hearth. The working doors are closed and the fire-door opened and the charge allowed to heat up, being slightly rabbled once or twice during the first hour. More air is now admitted and the charge is frequently stirred until, after about four hours from the beginning of operations, it is judged that the roasting is sufficiently advanced.

The grate is now cleared, fresh fuel thrown on, the damper opened and a brisk fire got up; the ore lying towards the back of the furnace is raked towards the fire-bridge and the reactions of smelting soon set in. The charge is rabbled vigorously; if it shows signs of fusing, a little lime is thrown in; if, on the other hand, it is too much cooled during the rabbling, the doors are closed and the fire urged. Lead flows into the well and the first tapping is made about three hours after the onset of the reaction-period. The operations of roasting and smelting are now repeated until the flow of lead slackens, when the residual slags are raked out of the furnace through the middle back door, and the lead is tapped again. The skimmings from the lead pot are returned to the furnace. The smelting period lasts about five hours, the consumption of coal is 40 p.c. of the weight of the ore, that of lime, 2 p.c.,

and 80 p.c. of the lead in the charge is extracted. A greater yield could be obtained by reduction of the residual slags in the furnace with coal, but it is more economical to smelt these separately in the blast furnace.

There are many variations of the English method of smelting. Sometimes, the slags are removed in the molten condition, their liquefaction being effected either by the addition of a fluorspar flux, or simply by raising the temperature high enough. The latter case is well described by Farey¹) in his account of reverberatory smelting in Derbyshire.

"The molten lead is collected in the bottom of the furnace, and the slag swims on the top to the depth of two or three inches. The tapping is then effected by poking out the stopping of lime, when the slag flows out like melted glass. It soon cools on the stone floor of the building. In the solid state it is opaque, of a whitish-grey colour, and moderately heavy. It is sometimes used for road metal. When the bulk of the slag has run off, the smelter proceeds to scatter upon the melted lead two or three shovelfuls of quicklime, in the state of powder, which has the effect of stiffening the portion of the slag which was left. He then draws it carefully off the metal, and rakes it upon the floor in a semi-fluid state. This is called drawn-slag, and is, when cold, of a very dark or black colour, and very heavy. The lead pan is now cleared out, if necessary, and, the stopping of lime being removed, the lead is suffered to run out of the furnace into the pan, where it is skimmed, the dross being thrown back into the furnace."

Variations in materials, locally accessible, and in the composition of the ores, naturally produce modifications of method. Thus, a reverberatory furnace, used for centuries in the South of Spain and known as the *boliche*, was adapted for the burning of wood. The fireplace was without grate and projected from one side of the hearth; the hearth sloped towards the one working door, situated near the fire-bridge,

¹ *General View of the Agriculture and Minerals of Derbyshire*, 1815.

and the well was close to this; a wide flue-chamber interposed between the hearth and the chimney-flue for the purpose of regulating the draught. Instead of lime, ashes and cinders from the ash-pit were used for drying and setting-up the charge after smelting.

The method used in the Cornish or Flowing furnace is of interest in that it combines the reactions of iron-reduction with those of air (and carbon) reduction. It was applied in Cornwall for the treatment of copper-bearing galena containing 60 to 70 p.c. of lead, and in Wales, and elsewhere, for the reduction of grey slags and other lead residues. Roasting and smelting in the Cornish process were carried out in separate furnaces. The charge of $1\frac{1}{2}$ to 3 tons was introduced into the calcining furnace through a hole in the roof, ordinarily closed by a slab, and roasted from 15 to 18 hours at a high temperature. It was then raked through openings in the furnace bottom into a vault below and transferred thence to the flowing furnace. This was rectangular and longer than the roasting furnace, with two working doors at each side, and a flue-door at the end opposite the firebridge. The hearth sloped towards the well near the second front-door, beneath which was the tapping pot and a small pit for the slurry. On this hearth, the charge of 2 tons of roasted ore was melted down in 2—3 hours and the lead tapped; the residues were then thickened by the addition of lime and culm (anthracite slack) and set up on the higher part of the furnace bed; 1 or 2 cwts. of scrap iron was thrown into the well and the charge again melted down. On tapping again, the lead flowed into the pot followed by the slurry (copper matte), which, collecting on the surface of the metal in the tapping pot, overflowed into the pit beneath. When the slag made its appearance, the lip of the pot was stopped with ashes and the slag diverted.

The whole operation of smelting lasted eight hours; the slag, as might be expected, was clean, containing only 0.5 to 1 p.c. of lead, and the matte was worked up to concentrate the copper and then sold to the copper smelters.

The *French* process, formerly used at Poullaouen in Brittany has points of resemblance to the Cornish, especially in the use of metallic iron during the smelting stage. The purpose of this is, however, somewhat different, since its chief function lies in the reduction of lead silicate, whereas in the Cornish method it aids in the separation of copper as a matte.

The ores contained 6 p.c. of silica, which necessitated long and slow roasting in order to prevent premature formation of lead silicate. The charge of 26 cwt. was thus roasted for 7 hours at a very low temperature, the crusts, rich in lead sulphate, being broken up frequently and stirred into the mass. When caking began (presumably due to the formation of lead oxide by reaction of sulphide and sulphate of lead) the temperature was raised until the mass became pasty. The first tapping was made about 5 hours later, the second after 2 hours or more. The residues, amounting to 30 p.c. of the charge and containing 40 p.c. of lead, were then drawn from the furnace and smelted with iron and other lead products and silver ores in a reverberatory. The yield of lead was 71 p.c. from the first treatment and 19 p.c. from the residue.

THE SILESIAN METHOD

Only a moderate extraction of lead is sought in this process, since the residues are smelted in the blast furnace. As in the English process, the furnaces are large, but the ore is roasted slowly at a low temperature and, consequently, the loss of lead is small. The incomplete reduction of the residues also results in the production of a much purer lead. The following is an outline of the method as employed at the Friedrichshütte, Tarnowitz. It has one feature of particular interest, in that oxidised compounds of lead, including flue dust, refinery litharge and the product of roasting a portion of the ores, rich in blende, in a long-bedded reverberatory, are added at a certain stage to the charge under treatment, whereby the roasting-period of this is appreciably shortened.

The furnace resembles in many respects the Flintshire as used at Couëron. It is rectangular, 16 feet long and 9 feet wide, with eight working doors; the hearth slopes gently to the sump and the well is at the end door near the flue. The passage from the furnace chamber to the flue is divided into four by brickwork partitions, in order to spread more effectively the hot gases which traverse the chamber. The ore is chiefly galena with 8 p.c. blende. The charge of $2\frac{1}{2}$ tons is spread on the hearth and roasted under the usual conditions. After 4 hours, the oxidised materials mentioned above, in quantity of half a ton or so, are added and stirred well in, the temperature is raised and the lead begins to flow. By the use of lime and the regulation of air supply and firing, the reactions of roasting and smelting are repeated two or three times and a tapping is then made. Another half ton of oxidised lead compounds is now added, the doors are closed, and a smoky flame produced by firing with small coal. The reducing atmosphere thus established brings about reduction of litharge to lead and of lead sulphate to lead sulphide, and the reaction of the last with oxide and sulphate of lead results in a further liberation of lead. This is tapped again at intervals, the whole period of smelting lasting seven hours; at the end of this the slags are drawn.

The consumption of coal is 40—50 p.c. of the charge; of lime, 1 p.c.; the extraction of lead is 60—65 p.c.; the residues are 30—35 p.c. of the weight of the charge and contain 40—45 p.c. of lead. This is nearly all recovered in the subsequent smelting of these and in working up the flue-dust, the actual loss being given as 1.5 p.c.

THE CARINTHIAN METHOD

This was used but rarely and is now extinct. It is characterised by the use of small furnaces, slow roasting of the ores and reduction of the slags in the furnace with coal. The furnaces used at Bleiberg, two of which were usually built side by side, discharging into the same chimney, are represented in the annexed diagrams, of which Fig. 5 is the front elevation

and Fig. 6 the horizontal section. The hearth is about 10 feet long and 4 feet 10 inches wide at the back near the fireplace, being thus about the same size as the old Derbyshire reverberatories. The width is maintained for about half the length of the furnace, when it is gradually reduced, until at

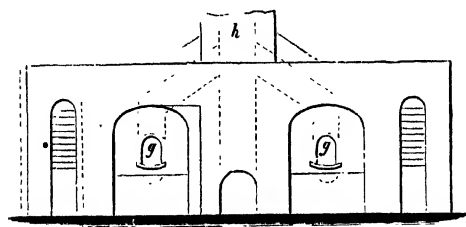


Fig. 5.—Bleiberg Furnace: Front Elevation.

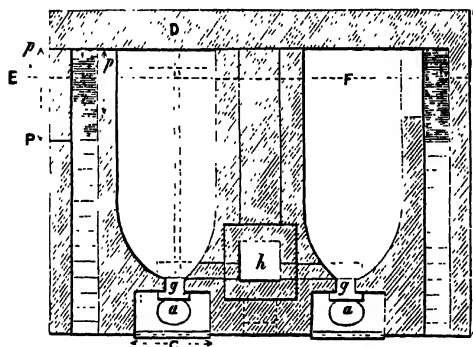


Fig. 6.—Bleiberg Furnace: Horizontal Section.

the working door *g* it is only one foot wide. The hearth is made of slags resting on a layer of beaten clay, and slopes from the back and longer sides towards the door; below this is a spout by which the metal flows from the hearth into the heated iron pan *a*. The fireplaces are built along the sides of the furnace and the gases are drawn into the chimney *h* by a flue above the working door. Wood or brown coal is the fuel employed.

The charge is a small one ($3\frac{1}{2}$ cwts.) and is spread in a layer only an inch or so thick; roasting occupies 3 to 4 hours and the smelting period lasts about the same time. The slags are then dried up by the addition of ashes and breeze and withdrawn. Another charge is let down and worked off in the same manner, but the residual slags are left in the furnace and the slags from the former treatment are added. The combined slags are then heated strongly and reduced (the process being known as *Bleipressen*) by means of charcoal, the operation lasting 7 to 8 hours and yielding about the same amount of slag lead (*Pressblei*), namely 150 lbs, as is produced by the smelting of one charge. The complete working-off of two charges occupies 22 hours and the yield of lead is 2.5 p.c. below that of the dry assay. The residues from the slag-reduction are relatively poor in lead (3 to 9 p.c.): they are concentrated to 50 p.c. by crushing and washing, and worked off either with the ore-charges or by a separate treatment of slag-reduction.

The *Missouri Air Furnace*, used for the smelting of high-grade galena is somewhat similar to the Bleiberg furnace. The hearth slopes towards the narrow end, where the discharging door and lead pan are situated. At the opposite end is another door for charging and rabbling. Wood is the fuel employed and the fireplace is built near the discharging door, the bridge being only about 1 foot distant. The hot gases escape up a pipe-chimney near the working-door. The method of working differs, in that the charges are much larger (14 cwts.) and reduction of the slag is omitted.

EXTRACTION OF LEAD IN THE ORE HEARTH

This method of smelting, though it lacks the apparent chemical simplicity of the reverberatory process, is much earlier in point of origin. It was almost eclipsed in certain lead-smelting districts, e.g. Derbyshire, after the introduction of the reverberatory, but it held its own in other places, and the progress of time has shown that, even in its original form,

it has powers of survival which the reverberatory method does not possess. Like the latter, it is applicable only to rich ores, containing at least 68 p.c. of lead, and it gives rise to residues, grey slags, of similar high lead-content, which require separate treatment in order that the metal may be recovered from them.

The construction of the furnace and the method of working are, however, very different, the method in broad outline, being as follows. The charge of ore, mixed with fuel, floats on a bath of molten lead and the air is supplied by a blast. The reduced lead trickles through the charge into the bath and overflows thence into an iron pot outside of the furnace. The lumps of grey slag are picked out and removed as they are formed and fresh quantities of ore and fuel are added, as required, in small charges. The method has the advantage that it is easily started and stopped, and so is suitable where the supply of ore is intermittent; it gives a good yield of pure lead in a short time, and the method of collecting this in the pan beneath has the merit of cooling the metal quickly after its liberation. On the other hand, even with the most careful manipulation of the blast, the furnace becomes hot and has to be laid off to cool for 6 hours, after working for about the same time; the loss by volatilisation is great and necessitates the attachment of efficient fume-collecting appliances to the plant. By reason of this high volatilisation, the process is not well adapted for ores rich in silver. The arrangement of the furnace is such that the blast blows directly towards the operator, so that the work is of an unhealthy nature. This objection is overcome, or at any rate mitigated, by placing the hearth under a hood, thoroughly ventilated, and by closing the front with a shutter in the intervals when manual operations are not being performed.

The chemical aspect of the process has many points of interest. The sulphide ore is in contact with carbonaceous fuel, and the mixture is permeated by the air-blast. Oxidation of the lead sulphide necessarily takes place, and in so far as it does, the ore is its own fuel. Oxide and sulphate of lead

are formed from galena at a high temperature and, as a result there is inevitable reaction according to the methods of air-reduction. Whilst, however, in the reverberatory process, these reactions of oxidation and reduction are, in the main, separate in point of time, in the one hearth they occur simultaneously.

The presence of the glowing carbonaceous fuel, and the carbon monoxide derived from it, introduces a chemical factor, in this case, which is lacking in the reverberatory method. By their agency, lead oxide is reduced to lead, and the reactions of air-reduction are thus supplemented by that of carbon-reduction. It is impossible to say to what extent the individual reactions are responsible for the yield of lead, for the conditions in the charge, with respect to temperature and composition, vary from place to place and are constantly being changed. Part of the oxidation, too, takes place on the workstone. It might be expected that the formation of lead sulphate from galena would not be favoured in the circumstances, and that the removal of the small amount that is produced would be facilitated by its reaction with carbon, whereby, according to conditions, lead sulphide is regenerated, or lead, or lead oxide is produced.

The chemical data bearing on this subject, though meagre, tend to support this view. The grey slags are heterogeneous and contain metallic lead. Percy (p. 282) found that the slags, separated from lead shots, contained only 2.4 p.c. of sulphur, present as sulphide and sulphate. Analysis of a sample from the Leadhills gave: $\text{PbS} = 5.6$, $\text{PbO} = 42.5$, $\text{SO}_3 = 2.8$, $\text{CaO} = 4.1$, $\text{ZnO} = 1.0$, $(\text{Fe}, \text{Al})_2\text{O}_3 = 18.2$, $\text{SiO}_2 = 26.0$. Total = 100.2 p.c. (Total S = 1.8. Pb = 44.3). As there is twice as much lime as is equivalent to the sulphur trioxide, it is unlikely that this sample contained much lead sulphate. A sample from Joplin¹) contained Pb = 12.7, PbO = 37.3, $\text{SO}_3 = 1.4$, S(sulphide) = 3.6, CaO = 11.5: one from Collinsville, Pb = 46.0, S = 3.5, CaO = 9.0. Finally,

¹ Quoted in Hofman, *Metallurgy of Lead*, p. 117.

partial analyses of grey slags from the hand hearth and the mechanical hearth gave¹):

| | Pb | S | CaO | FeO | Insoluble |
|-----------------------|------|-----|-----|------|-----------|
| Hand hearth | 45·0 | 2·6 | 9·0 | 12·2 | 12·2 |
| Mechanical Hearth . . | 43·7 | 1·9 | 9·9 | 12·8 | 12·6 |

Newnam reckons that these slags contain 8·5 p.c. of metallic lead and 6 p.c. of lead sulphide, whence it follows that $PbO = 32·4$ and $SO_2 = 2·6$ p.c.

In all these cases, the total amount of sulphur is very small, and even if it were all present as sulphate, which it is not, would not be equivalent to the lime. Though most of the analyses return the sulphate in the form of lead sulphate, there cannot be any reasonable doubt that it is mainly present as calcium sulphate.

In the treatment of material other than sulphide ores, for example: flue dust, lead ashes, spent peroxide from accumulators, etc. the reaction of carbon-reduction naturally plays a very important part.

The application of the hearth process to ores varies somewhat according to the nature of these. It was once customary to smelt the ores from each vein apart, when they could be obtained in sufficient quantity, and this was probably an indication of peculiarities in practical working dependent on composition. Similarly, ore-concentrates of different size, sieve ore, smiddum (grit) and slimes, were treated separately. It is a common practice still to submit the ore to a preliminary roasting process (flash roast) before smelting in the hearth. This method has the advantage of economy, as coal is saved, the smelting done more quickly, and the lead is purer and needs less refining.²)

¹ W. L. Newnam, *Trans. A. I. M. E.*, 1916, 2139.

² Westgarth Forster, *Section of the Strata, etc.*, 3rd. Ed. 1883, p. 190.

The roasted ore is also said to work drier in the ore-hearth. Something, in this matter, depends on the nature of the ores, for certain kinds appear to profit more by this treatment than others. Comparative data are given in the following table, and are the results obtained in smelting 400 tons of ore, yielding, on assay, 81 p.c. of lead, one half of which was smelted raw and the other half after roasting.¹)

| | Roasted ore | Raw ore |
|---------------------------------------|-------------|---------|
| Lead, first fire | 73·1 | 60·8 |
| Lead in grey slags | 2·5 | 1·8 |
| Lead in fume loss, hearth-ends etc. . | 5·4 | 18·4 |
| | 81·0 | 81·0 |

In the case of ore-slimes, preliminary roasting and sintering are almost essential, since the fine material is liable to be blown away by the blast.

The furnace used for roasting is of the reverberatory type but with a flat hearth 6 feet square. The charge of ore is 1 bing (8 cwts.) and this is introduced through one of the working doors and spread to a depth of 2 to 3 inches. The firing is gentle at first and the ore stirred at intervals: later the temperature is raised to dull redness and the charge vigorously rabbled until it becomes clammy; it is then withdrawn. Three charges are worked off in 8 hours; 2 men attend the furnace and the consumption of coal is 1·5 cwts. per bing of ore.

The Ore Hearth or Scotch Hearth is represented in vertical section in Fig. 7.

Its main component is a pan made of iron, 3 inches thick, which rests on sand and holds 30 cwts. of lead. The bottom of this, *A*, is 22 inches square and the depth is 4·5 to 6 inches or even up to 12 inches. In front of this is a working plate, known as the workstone, *B*, formerly separate, but now cast

¹ Cookson, *Local Government Report*, 1878—9, 289.

on to the front edge of the pan. This is 3 feet long, 18 inches wide and 2·5 inches thick and slopes downwards, the total fall being 4 inches; it is embedded in fireclay, or a mixture of slime ore and bone-ash and has a raised border, about 1 inch high, along the two sides and front, and a channel two inches wide and 1 inch deep diagonally across it. The lead, running

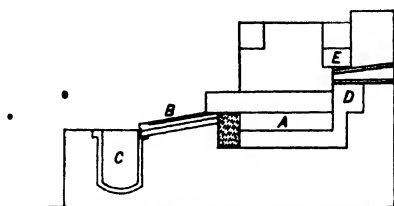


Fig. 7.—Vertical Section of the Ore Hearth.

from the pan along this channel, is received into an iron pot, C kept warm by a small fire beneath. At the back of the hearth is an iron prism called the backstone, D, 28 inches long, 5 inches wide and 6·5 inches high, and above this is a similar prism, E, the pipestone, with a hole for the bellows-pipe; both 'stones' are sometimes cast in one piece. The blast pipe is 6·5 inches above the level of the upper edge of the workstone, but it often sags an inch or two after the furnace has been working some time; the direction of the blast is towards the top of the workstone.

The top of the hearth is finished level with masonry, upon which the 'hearth ends' (particles of ore flung out by decrepitation, or blown out by the blast) are collected. The whole stands under an arch of masonry, opening at the back into a flue which leads to the fume chambers; at the side of this is a feed door, giving access to the hearth, and allowing of the detachment of adhering slags and the placing of a peat in front of the blast-pipe.

Wood, peat or coal may be used as fuel. To blow in, the hearth is filled with peats, one is kindled in front of the blast-pipe and the blast turned on. Small quantities of coal are

added and then, preferably, small charges of browse (the fritted mass of ore, slag, and fuel from a previous operation), or, failing that, roasted ore. Suppose that the fire has been made up and a fresh charge of ore added; the shutter is let down for about 5 minutes, then raised, and the charge stirred by thrusting a poker into the metal bath and levering the whole mass up. Part of the material is thus brought on to the workstone, where it is examined by the smelter, the grey slags removed with a small shovel and thrown into the water-pit, and the fritted lumps of browse broken up. If the browse is pasty, a little lime is sprinkled on it before returning to the hearth. The helper, or shoulder-fellow, clears an opening for the blast, and places a peat in front of the nozzle, so that the air may be distributed while the peat still remains, and may have unimpeded passage when it has burned away. The browse is returned, the fire made up, and a fresh charge of ore put on.

Some points of practical importance are¹): 1) the blast should be well divided and not restricted to a few channels, and it should not be stronger than suffices to smelt the ore; 2) the charge should be stirred frequently and the lumps of browse broken up; oxidation of this on the workstone is most important, for the lead always flows freely after the return of the browse; 3) the quantity of lime should be limited, and also the amount of coal; excess of the latter increases the bulk of browse.

Such a furnace has a capacity of 40 cwts. of ore on a 12 hour shift or 240—280 cwts. per week; the yield of lead is 70 p.c. of the ore, and for the production of 1 fodder (21 cwts.) of lead, 1.5—2 cwts. of coal, 1 cart-load of peat and 3 bushels of lime are required.

There are many modifications of the Scotch — or Ore — Hearth, designed with the object of preventing the over-heating of the furnace and, consequently, of making it continuously

¹ H. L. Pattinson, *Trans. Nat. Hist. Northumberland, Durham and Newcastle*, 1838, **2**. 152.

workable, or in order to economise fuel by utilising the waste heat for heating the blast. Cooling may be provided in various ways. The pan may be supported on pillars instead of being embedded in masonry, so that it is cooled by the circumambient air, or it may be built in a jacketed form and cooled by the circulation of water or air. When, in the latter case, air from the blower is sent through the jacket, the blast is heated and an economy of fuel effected, but the loss of metal by volatilisation is increased, which is a disadvantage unless it is desired to use the fume for the making of a pigment. Such a method of air-cooling was adopted in the Rossie hearth, in which the jacketing extended along the back and both sides of the pan. This furnace is now obsolete.

In the Missouri district, preference was given to the American Water Back Ore Hearth, and the Moffet, or Jumbo, Hearth, but these are now nearly ousted in favour of sintering and smelting in the blast furnace. The first of these has the three sides of the furnace formed of a cast-iron jacket through which water circulates; the blast chamber is at the back of the jacket, and the arrangement ensures the castings and tuyeres (of which there are three) being kept cool. The lead pan is set in brickwork.

In the Moffet, or Jumbo, hearth, the lead pan is set on pillars and exposed to the cooling action of air. Two furnaces are built back to back, a chamber cooled both by air and water separating them; the blast is heated by passing through the air chamber. The hearths can be worked independently; one flue is common to both.

Until comparatively recently, little had been done to increase the size of the ore-hearth which, in its original form and modifications, has been restricted in length to about 4 feet. The introduction of mechanical rabbling by Newnam at the St. Louis Smelting and Refining Works, Collinsville, Ill., has made it possible to double the length of the hearth. This St. Louis or Newnam hearth merits a more detailed description.

THE NEWMAN ORE HEARTH

The pan is 8 feet long, 20 inches wide and 8 inches deep; it is made of iron, jacketed at back and sides, the bottom being freely exposed to air and not jacketed. Along the front is the workstone or apron, 2 feet wide, sloping slightly and provided with a rim around the edges. Unlike the hand-hearth, the lead does not flow from the pan across the workstone to a well in front, but escapes by means of a syphon tap, near the back of the pan, into a small basin, whence it overflows through a spout and is run directly into moulds. Along the back are 16 tuyeres, equally spaced, each 2 inches in diameter, and situated 2 inches above the top of the pan. The blast from these is directed slightly downwards. The hood is two-fold, the inner one, over the lead pan, being connected to the exhaust and leading to a Lodge fume-condensing plant, the wider one, outside this, discharging into the air.

The mechanical rabble works in front of the furnace. The rabble-arms are hung from a carriage travelling on an overhead track, and their motion is similar to that of the hand-rabble. They work in one direction only, and each time the rabbles are withdrawn from the charge, they are carried forward 4 inches by the carriage and are then in position for the next stroke. A 'helper' follows the rabble with a long-handled shovel, pushes back the loose charge and picks out the grey slag; behind him comes a 'charger' who spreads fresh ore and fuel. At the end of a trip, the rabbling machine is returned, without rabbling, to the other end of the furnace and the operations are repeated.

With this arrangement it has been found possible to double the length of the hearth without increasing the manual labour required to work it; at the same time, the consumption of fuel is halved, and the production of fume and dust is greatly diminished. The following results are averages for an 8-hour shift, over a period of 4 weeks, for an 8-foot Newnam and a 4-foot hand hearth worked side by side, the labour

being the same in each case. The ore consisted of galena concentrates containing 72.5 p.c. lead and 15.1 p.c. sulphur.

| | Newnam hearth | Hand hearth |
|-----------------------------|---------------|-------------|
| Dry ore charged | 13,179 lbs. | 5,091 lbs. |
| Pig lead produced | 6,443 " | 2,030 " |
| Grey slag | 3,318 " | 1,329 " |
| Dust and fume | 2,328 " | 1,481 " |

Distribution of lead in the products:

| | | |
|--------------------------------------|------------|------------|
| Pig lead | 67.44 p.c. | 55.00 p.c. |
| Grey slag | 15.18 " | 16.20 " |
| Dust and fume | 17.38 " | 28.88 " |
| Consumption of coke breeze | 3.6 " | 8.8 " |
| Elimination of sulphur of the charge | 87.9 " | 80.6 " |

It is claimed that the cost of production of lead from rich ores and concentrates by this process is much below that for sintering and blast-furnace smelting.

A test run made on high-grade galena ($\text{Pb} = 82$, $\text{S} = 11.2$ p.c.) gave the following results on an eight hour shift, with a consumption of 2.4 p.c. coke breeze and 2 p.c. crushed limestone (used in place of slaked lime).¹

| | |
|---------------------------|-------------|
| Dry ore charged | 14,436 lbs. |
| Lead contents | 11,837 " |
| Pig lead made | 10,790 " |

The distribution of lead in the products is:

| | |
|-------------------------|--------------|
| Pig lead | 91.15 |
| Grey Slag | 4.25 |
| Dust and Fume | 4.60 |
| | <hr/> 100.00 |

The yield of pig lead for a similar ore worked on the hand-hearth would be 80—85 p.c.

CHAPTER V

EXTRACTION OF LEAD IN THE BLAST FURNACE

Smelting in reverberatories and hearths is restricted to high-grade ores and concentrates, containing over 60 p.c. of

¹ W. E. Newnam, *Trans. Amer. Inst. Min. Eng.*, 1916, 2139.

lead and less than 5 p.c. of silica. Ores not conforming to this standard of composition, as well as slags from the air-reduction process, roasted mattes and furnace products rich in lead are smelted in the blast furnace. Surface ores, or similar mixtures of sulphide and oxidised compounds of lead, may be smelted direct; ores which consist largely of sulphides must first be roasted to remove the sulphur and convert the lead into oxide (and sulphate), and the roasted product is then smelted with reducing agents, fluxes being added, if necessary, in order to slag the earthy and silicious materials of the charge. If the charge contains much sulphur this is not, as a rule, eliminated under the conditions existing in the blast furnace, but it enters into combination with iron, copper, and lead to form a matte. As the complete removal of sulphur from an ore by roasting (*i.e.* dead-roasting) is a difficult and expensive operation, and as many lead ores contain copper, some cupriferous matte is generally produced in blast-furnace smelting, and from this matte the copper can be recovered by suitable treatment. The residual sulphur of the charge thus serves as a means of extracting the copper, and is itself removed in effecting that end; from a practical point of view, too, the production of a small quantity of matte is advantageous, in that it promotes the easy running of the furnace and gives cleaner slags.

The chemical reactions, already described, by which lead is produced from its compounds under metallurgical conditions, are all operative in the blast furnace, though to an extent which varies considerably according to conditions and the composition of the charge. The roasting-and-reaction process is generally quite subsidiary, for the atmosphere in the furnace is essentially a reducing one, and oxidation of sulphide to sulphate, necessarily, does not take place to any great extent. 'Reaction' between sulphide and sulphate, however, is always possible in the hotter parts of the furnace, when both compounds are present in the charge.

Reduction of galena by iron, or precipitation, is at times an important reaction in the blast furnace, though it carries

with it the same drawbacks as were encountered in reverberatory smelting, viz. the production of excessive amounts of matte, which demands costly treatment for the recovery of lead and copper contained in it. Formerly, metallic iron was added to the charge; now it is customary to add oxide ores of iron, roasted matte, and iron slags, *i.e.* materials reducible in the furnace to iron, which is then available for reaction with lead sulphide. With the present methods of smelting, however, the importance of these ferruginous materials is based rather on their slagging properties and their power of replacing lead by iron in its silicate, than on their suitability for bringing about the reaction of iron-reduction of galena.

The typical reaction of blast-furnace smelting is reduction of lead oxide by carbon (and carbon monoxide). Thus the smelting of sulphide ores of lead necessitates two very distinct operations: roasting of the ores to convert the lead into oxide, the sulphur being driven off as volatile oxides; and reduction of the roasted ores in the blast furnace. In no case is roasting complete, in the sense that all the sulphur is burnt off and all the lead left as oxide. The roasted mass always contains some unaltered sulphide of lead (the amount of which compound may be supplemented by subsequent reduction of sulphate), and lead is also present as sulphate and silicate. It should be added that arsenic, to a large extent, and some antimony, if these metals are present, are volatilised during the roasting.

ROASTING OF THE ORES

The old method of roasting in heaps is sometimes, though rarely, used for pyritic ores poor in lead. The construction of the heaps is simple. The ground is first cleared and levelled, a bed of fine ore is laid down, and then the wood for kindling the heap. Upon the wood, the ore is piled; first, the main bulk of coarse ore, above this the fines and, over all, the slimes, the whole forming a pyramidal heap which may vary very greatly in dimensions. At Port Pirie, N.S.W., the heaps are 250 feet long, 20 feet wide, and

6 feet high, the material being ore-simes which are dried and cut into blocks. The sulphur-content is reduced from 12 to 7 p.c. by this treatment.

Ores from the Lower Harz, rich in blende and pyrites, not suitable for reverberatory roasting, were roasted in heaps containing 300—500 tons three times. The first roasting lasted six months, the second 6—8 weeks, and the third 4—6 weeks. After dismantling a roasted heap, the fines were extracted with water, or dilute sulphuric acid, in order to remove zinc sulphate. In this way, the sulphur content could be brought down from 18 to 4 p.c. Mattes are also, sometimes roasted in heaps, smaller than those used in the case of ores. The detrimental effect of the roasting gases on the surrounding country is an important consideration in heap roasting: it is estimated that four square miles of land are affected by a heap from which 25 tons of sulphur escapes daily.

Shaft furnaces are occasionally employed in roasting pyritic lead ores, such as the 'mixed ores' of Oker, which contain galena 11, blende 28, pyrites 25, chalcopyrite 15, barytic gangue 21 p.c. These are put through kilns, whereby the sulphur is reduced to 10—12 p.c. and then roasted in heaps down to 6—7 p.c. of sulphur. Dust furnaces (*Schütt-öfen*) sometimes find application, as at Freiberg, where lead-bearing pyritic ores, containing galena 18, pyrites 60, gangue 22 p.c. (total sulphur, over 25 p.c.), are roasted in Gerstenhöfer furnaces, until the sulphur is reduced to 6—7 p.c.; the product is then finished off in reverberatories. These ores are also roasted in muffle furnaces of the Hasenclever type, when it is desired to utilise sulphur dioxide for the manufacture of sulphuric acid. Wedge furnaces, commonly employed in America for the roasting of copper ores, find application also in the roasting of lead ores. These are shaft furnaces with seven, circular, superimposed hearths, and mechanically worked rabblers.

Roasting in Cylinder Furnaces.—There are two types of revolving cylinders, the rotation being either about a hori-

zontal or a sloping axis. The Brückner cylinder exemplifies the first type. The dimensions of these cylinders vary from 12 by 6 feet to 26 by 8 feet, the charges for these being 4 and 25 tons respectively. They make one revolution in 40 minutes and are supplied either with stationary or movable fire-boxes, the latter being preferable when roasting proceeds of itself after ignition of the ore. The time taken to work off a charge varies from 3 to 24 hours, according to the nature of the materials.

The Oxland cylinder is an example of the second type. It is used at Laurium, in Greece, for roasting concentrates containing Pb, 60 p.c.; S, 20 p.c. This furnace is 42 feet 9 inches long, 3 feet 1 inch diameter inside; it makes one revolution in 4 minutes and roasts the ore down to 4 p.c. of sulphur.

ROASTING IN REVERBERATORY FURNACES

Of the older methods of roasting, the reverberatory is the best. The furnace is the easiest to handle, in so far that the temperature can be quickly raised or lowered. As the ore is heated from the top, chiefly by radiation from the arch, there is little risk of the charge fritting and sticking to the hearth, as may happen, for example, in the muffle furnace. Many of the factors involved in the construction of the furnaces, and in the conduct of operations, have already been considered, but it may not be out of place to recall and amplify them here. The galena must be finely divided, and the temperature must be regulated so that incipient fusion of the mineral is avoided, otherwise the fritted material becomes impervious to air and oxidation is arrested. With progressive conversion of sulphide into oxide and sulphate, the risk of fusion is lessened; at the same time, it is desirable that the temperature should be increased, in order to hasten the oxidation of the unaltered sulphide. The advantage of a temperature-gradient in the furnace, coupled with the transportation of the charge, as oxidation progresses, from the cooler to the hotter parts, becomes obvious.

It may be remarked that the exothermal oxidation of the metal sulphides is itself a source of considerable heat, and permits of a much greater length of furnace than would be consistent with efficiency, were the heating entirely derived from the combustion of the fuel. Ample provision must of course be made for the admission of air and for the removal of the gases produced in roasting. The cooler air entering the furnace-chamber tends to form a layer between the surface of the charge and the hot gases sweeping the arch in their passage from the grate to the flue; the oxygen which this air carries, is therefore available on its lower surface for oxidation of the ore, and on its upper surface, for the completion of the combustion of gases from the fire, thus generating a further supply of heat within the roasting chamber itself. Frequent stirring of the charge is essential, not only to expose fresh surfaces to air, but to liberate the imprisoned sulphur dioxide, which by its action on many of the oxidation products reverses the roasting reactions and thus delays the process. Mattes, as well as ores, may be roasted in the reverberatory, in general, they require a higher finishing temperature. Mechanical reverberatories, such as those used in roasting copper ores, find a somewhat limited application for the roasting of lead ores. Of these furnaces, some have fixed hearths and movable rabbles, *e.g.* the Wethey, Ropp, and Keller furnaces; others have revolving hearths and fixed rabbles, *e.g.* the Brunton, Heberlein, and Godfrey furnaces. It will suffice for our purpose to describe one of these briefly, and the Ropp Straight Line furnace will be selected as the one which has, perhaps, found most favour in the treatment of lead ores. Reference to the annexed diagram (Fig. 8) will help to make clear the description.

The Ropp is a rectangular furnace with 3 or 4 fireplaces disposed on one of the long sides. Four or six rabbles work on the hearth. The ploughs which stir the ore are set at an angle of 45° to the rabble arms. These are attached to a vertical rod passing through a slot $1\frac{1}{2}$ inches wide which runs continuously down the middle of the hearth. An endless

wire rope, driven by power, links up these arms and passes round two pulleys at the ends of the furnace. The complete revolution of the rabblers takes $3\frac{1}{2}$ minutes, and as they are outside of the furnace for more than half that time, they become cooled and preserved thereby from injury. At each end of the furnace are swinging doors, through which the rabblers enter and leave the furnace. The working doors are placed at suitable intervals along the longer sides of the furnace. The ore is charged at one end of the furnace, traverses it in the direction opposite to that of the hot gases,

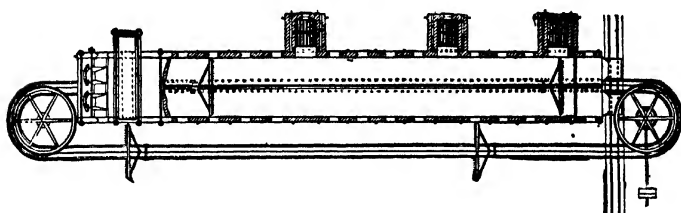


Fig. 8.—The Ropp Furnace.

(From Schnabel's 'Handbook of Metallurgy,' Macmillan & Co., Ltd.)

and is discharged at the other end, remaining in the furnace 6—8 hours. The length of the hearth varies from 100—150 feet, the width from 11—14 feet, in the clear; the large furnaces put through 50—80 tons of ore in 24 hours, with a coal consumption of 13 p.c., and an expenditure of 5—8 h.p. for working the rabblers.

The use of mechanically-rabblled furnaces for roasting lead ores suffers, however, from certain disadvantages. Many of the conditions necessary for the successful roasting of galena, which were outlined above, are best attained in the long-bedded, hand-worked reverberatories (*Fortschaufelungs* furnace), and these furnaces have been, and still are, extensively used for roasting lead ores.

The construction of this furnace is illustrated in Figs. 9 to 13.

Fig. 9 is a front elevation of the furnace, which is constructed of brickwork with a lining of fire-brick, and stayed

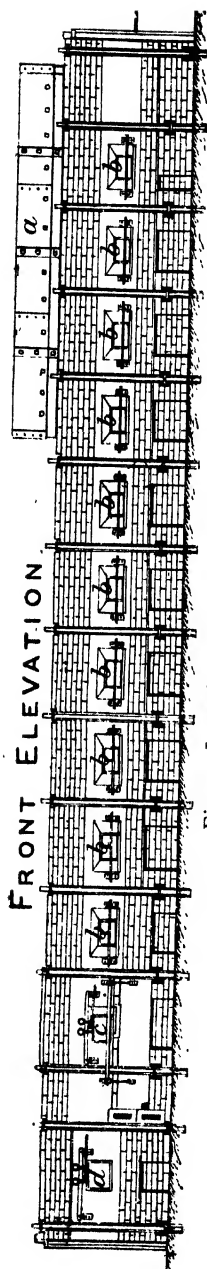


Fig. 9.—Long-bedded Roasting Furnace.

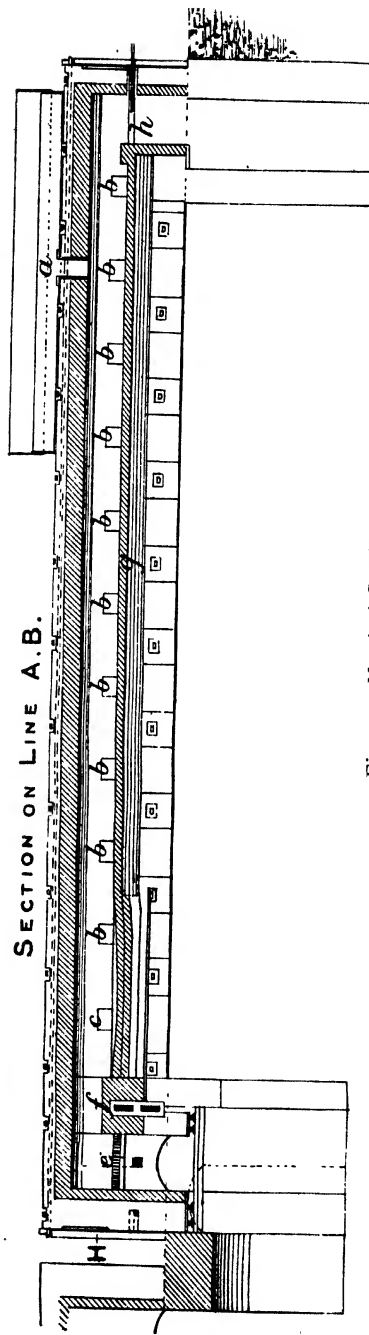


Fig. 10.—Vertical Section.

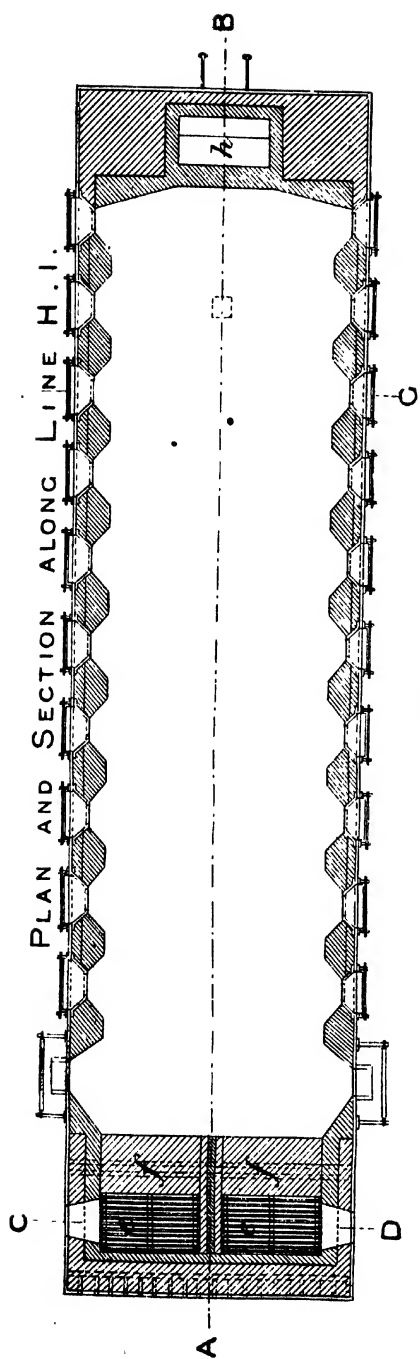


Fig. 11.

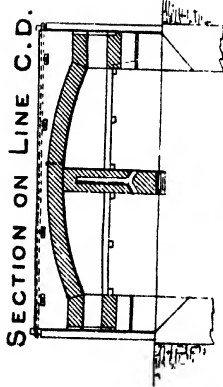


Fig. 12.

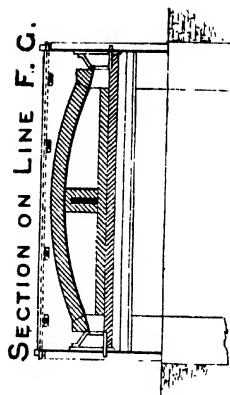


Fig. 13.

together with iron standards and crossbars. In this is also shown the hopper *a* for charging the ore, the ten working doors *b*, the door *c* for the withdrawal of the charge, and the door *d* for charging the fuel.

Fig. 10 represents a vertical section, showing the fire-grate *e*, the fire-bridge *f*, and bed of the furnace, constructed of iron plates supported by pillars of brickwork, which are cooled by circulation of air below; upon these plates are built the materials composing the bed of the furnace. *g* is the opening in the roof through which the ore from the hopper is discharged into the furnace bed, *h* the flue leading to a series of condensing chambers.

Fig. 11 is a plan of the furnace, and Figs. 12 and 13 are vertical sections through *cd* and *fg* respectively.

The usual size of these furnaces is 60 feet by 16 feet; occasionally they are much longer—up to 80 feet—but the breadth is limited by the necessity of working the charge from each side. The bed of the furnace is sometimes divided into four hearths, each with a step of 2 inches towards the fire-bridge, and having two working doors at either side. The ore is charged on the hearth furthest removed from the fire and spread out in a layer 3—6 inches thick. The roasted ore is discharged through an opening in the hearth nearest the fire-bridge, and the ore from each hearth is raked up in turn, so that it is subjected to a gradually increasing temperature as the oxidation of the sulphide proceeds. Sometimes the roasted ore is discharged as a powder, in which case it has to be briquetted before smelting; more usually it is sintered, a sump being provided near the fire-bridge (*v.* Fig. 10) in which the semi-fused mass is collected, and from which it can be raked into slag pots and agglomerated by tamping. When complete fusion is required (this is not advisable when the ores are rich in silver) the furnace sometimes has a separate hearth next to the fire-bridge, smaller, and at a lower level, than the main ones, and connected with them by a vertical flue about 2 feet 6 inches high. Sand may be strewn on the fusion-hearth before the charge is raked on. The effect of

this is to decompose the lead sulphate, lead silicate being formed on fusion and sulphur trioxide driven off. As lead sulphate is reduced to lead sulphide in the blast furnace, this method of treatment lessens the matte-fall. The charge is melted on this hearth, raked into slag pots and broken up before smelting. This method of treatment, slag-roasting as it is termed, is less favoured by smelters than sinter-roasting, which leaves the material in a porous condition suitable for the blast furnace. With a four-hearthed furnace of this description, the charge is rabbled every 20 minutes and moved down every 4 hours, the coal consumption is 21—25 p.c.: the loss of lead, without sintering, is 2.5 p.c., but when the charge is sintered it may be so high as 15—20 p.c. The loss of silver in the former case is negligible, but may reach 2—5 p.c. when the mass is sintered.

Heap-roasting may be combined with cylinder- or reverberatory-roasting, and any of these with the method of blast-roasting which will now be described.

BLAST ROASTING

In 1896 Huntington and Heberlein introduced a method of treating galena, and concentrates consisting of galena mixed with pyrites and blende; by this process the ore is rapidly desulphurised and obtained in a condition suitable for the blast furnace, and incidentally the sulphur dioxide produced may be utilised for the production of sulphuric acid. In this process the ore is mixed with 6 to 15 p.c. of lime or limestone, according to the proportion of sulphur in the ore, and roasted in a reverberatory furnace. The partially desulphurised material is transferred to a pear-shaped pot or converter, made of sheet iron, in which it is submitted to the action of a blast of air; during the blowing in the converter, energetic oxidation takes place, accompanied by other reactions, resulting in a rise of temperature sufficient to bring about agglomeration of the mass. This principle has been modified in various ways and has attained immense importance, during recent years, in the practice of lead-

smelting. The modifications are concerned with the materials added to the charge, and with the manner in which the air is supplied. In the original process, the air is blown upwards through the charge, and this arrangement is adopted in the Carmichael-Bradford and Savelsberg modifications, which are thus termed 'up-draught' processes. In the Dwight-Lloyd process, the air is drawn downwards, by suction, through the charge, and the term 'down-draught' is therefore applied to this process.

The converter used in the Huntington-Heberlein process is shown in Fig. 14.

The blast enters by a pipe at the bottom of the converter and the charge rests on a false bottom, consisting of an iron grate, which serves to distribute the blast. When in action, the top is covered by a hood through which the fumes escape; after the roasting is completed, the hood is removed, the converter tipped, and the agglomerated mass allowed to fall some distance in order to break it up. Such a converter takes a charge of 8 tons.

To start the operation, a small fire is lighted in the converter and some hot, partly-roasted ore added. A low-pressure blast is turned on, and then the main bulk of the ore, which may be either hot from the reverberatory roasting, or cooled and moistened with water, is added from time to time in suitable quantities, the blast pressure being increased. The method used at Braubach (Prussia) may be quoted as an example. The ores are roasted in reverberatories down to 10 p.c. of sulphur. The pots hold 11 tons. One ton of hot ore is put in first, then 5 tons of cold ore on top. After 8 hours blow, the remainder of the charge, 5 tons, is added cold, and the blow continued for 4 hours longer. The sulphur is reduced, thereby, to 3 p.c. One reverberatory serves $1\frac{1}{2}$ converters.

At Trail, British Columbia, a mixture of raw ores, concentrates, mattes from the blast furnace, and limestone, containing lead 40—44, zinc 10, iron 10—13, lime 7—10, silica 8—11 and sulphur 14—17 p.c. was first roasted two hours in

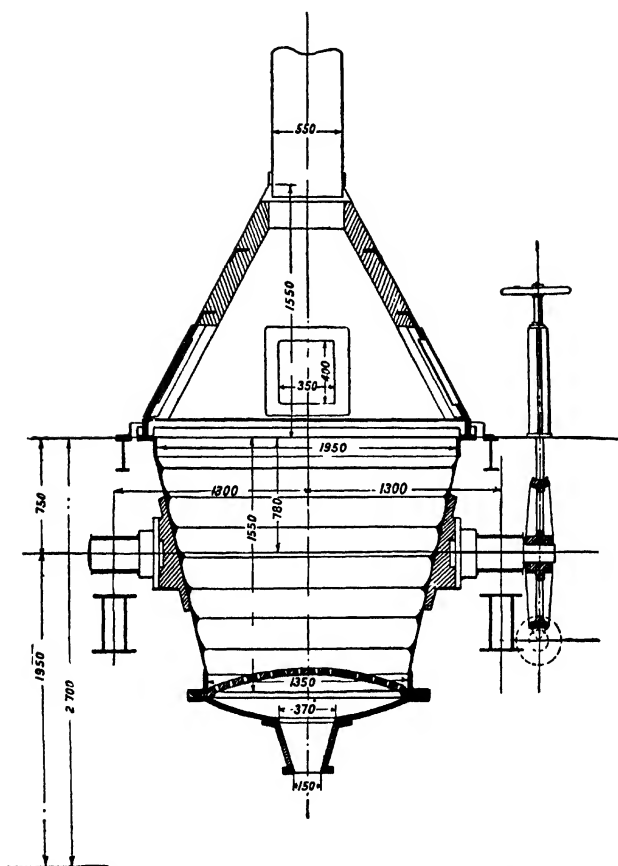


Fig. 14—Huntington and Heberlein Converter.
(From Collins' 'Metallurgy of Lead'. C. Griffin & Co. Ltd.)

a mechanical roaster until the sulphur was brought down to 8 p.c. and then finished off in a similar converter.

In the Savelsberg process, limestone and silicious materials are added to the ore and the mixture blown directly in the converter, the preliminary roasting of the charge being omitted.

The working is illustrated by the method used at Rams-

beck, Westphalia. The charge was made up of 100 parts of high-grade galena, 10 of quartzose silver ores, 10 of spathic ore and 19 of limestone and contained, on the average, 9 p.c. of sulphur. This was blown in a converter, bowl shaped, but similar in principle to the one shown above, a charge of 8 tons being worked off in 18 hours and the sulphur reduced to 2—3 p.c.

In the Carmichael-Bradford process, the preliminary roasting of the ores is likewise omitted. The materials are mixed with calcined gypsum and water, and after the mixture has set, it is broken up into small pieces and submitted to the pot-roasting process.

This method was at one time used at Broken Hill, which is favourably placed, in that gypsum occurs in the neighbourhood. The converters were pots 4 feet high and 6 feet in diameter, holding 4 tons. The ores were galena concentrates containing 70 p.c. of galena and 15 p.c. of blende, and slimes containing 24 p.c. of galena, 30 p.c. of blende and 23 p.c. of silica, which were mixed in the proportion of 1 to 3 with one part of gypsum, calcined at 200°. The mixture after wetting and setting was broken up and formed the charge for the converters. Sulphur was reduced from about 15 to 4 p.c. The gases, averaging 8.5 p.c. of sulphur dioxide and 0.4 sulphur trioxide, were converted into sulphuric acid, which was used in the separation of blende from galena by the Delprat process. This method does not appear to have been used elsewhere.

The chief shortcomings of these processes are that they are discontinuous, and the capacity of the converters is small. Only a comparatively thin layer of the ore is being oxidised at any particular moment, the main bulk remaining inert, either in an oxidised or unoxidised condition. These disadvantages are avoided in the down-draught method of Dwight and Lloyd, the essence of which is that a thin layer of fine ore is exposed to the air, and the process is continuous. As the roasting is quickly accomplished, the capacity of the machines is considerable.

One type of machine, in which the operation is carried out, is shown in Fig. 15. It consists of a continuous series of pallets, 42 inches wide by 24 inches long, composed of cast-iron grates with $\frac{1}{4}$ inch spaces. In the course of their revolution, the pallets pass beneath the charging hopper, and receive the moistened ore, which is spread about 4 inches thick; thence they pass to the fire-box, where the surface of the charge is ignited by a flame pointing downwards, and then to the suction-box, where the roasting is effected by air drawn through the charge. Finally the roasted ore is discharged automatically at the end of the machine by the fall of the pallets to the lower track; the empty pallets return in course of time to the hoppers, and the cycle of operations is repeated. One complete revolution is made in about 45 minutes.

The difficulty arising from the clogging up of the grates with sinter has been overcome at Trail by building the grates with 7 bars, set parallel to the direction of movement. These are cast with fingers, which fit into one another with a small clearance for the passage of the air. The outside bars and two of the inside ones are rigid, the three alternate bars are loose, and a rocking motion is thus set up as the pallet drops, which automatically cleans the slots in the grate. The adjustment of the grate bars is effected, if necessary, by means of a chisel, thrust between the fingers.

For the efficient working of this process, the sulphur in the charge should not exceed 18 p.c. In the treatment of concentrates, either preliminary roasting in a reverberatory is necessary, or the concentrates must be diluted with poor ores before being roasted by the Dwight-Lloyd process. By the adoption of a double roast, either in Huntington-Heberlein and Dwight-Lloyd converters, or in a double set of the latter it has been found possible to avoid reverberatory roasting and dilution; sulphur is reduced to 2—3 p.c., and in the subsequent smelting the yields of matte and slag are small. At Bunker Hill, mattes and ore concentrates rich in sulphur are first roasted in a seven-hearth Wedge furnace down to about

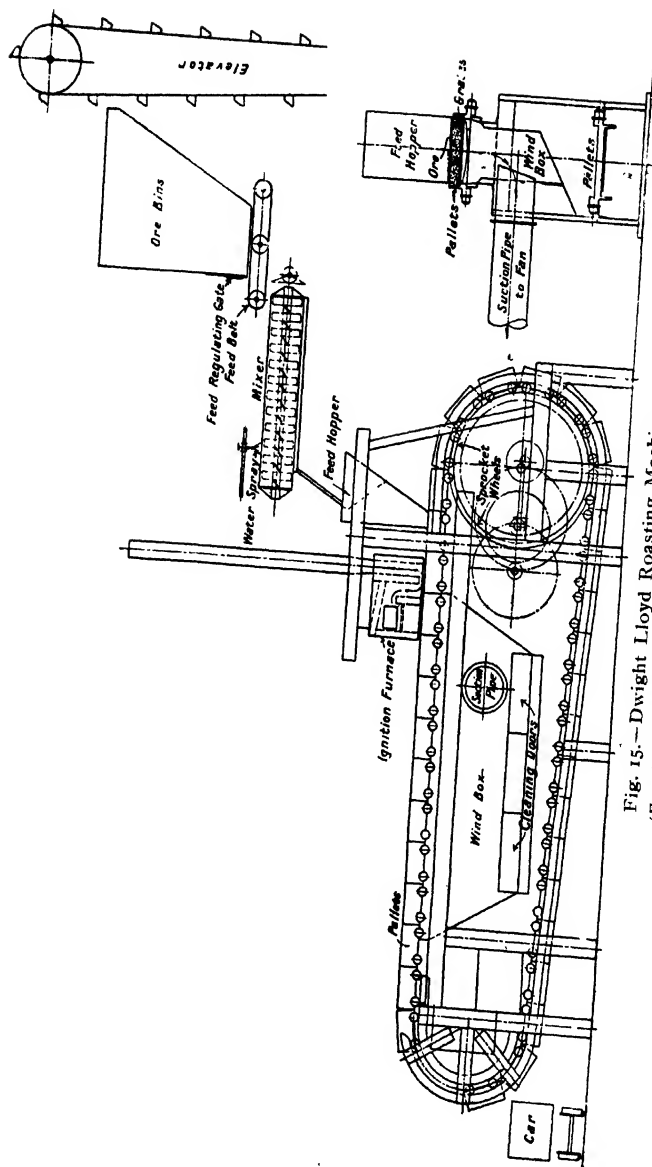


Fig. 15.—Dwight Lloyd Roasting Machine.
(From Collins' 'Metallurgy of Lead', C. Griffin & Co. Ltd.)

9 p.c. of sulphur. This furnace supplies 7 Dwight-Lloyd machines, each with a capacity of 80 tons per 24 hours. Formerly the matte-fall in the blast-furnace smelting of this material was 12 p.c.; this has been reduced by the adoption of the double-blast roasting treatment.¹⁾

Some idea of the composition of charge and sinter is given in the following table, which expresses the mean results of five months' working at Toole, Utah.²⁾

| | Per cent. | | | | | | | Ozs. per ton | |
|----------|-----------|-----|-----|------|--------|-----|------------------|--------------|-------|
| | Pb | Cu | Zn | S | Fe, Mn | CaO | SiO ₂ | Ag | Au |
| Charge . | 13·5 | 0·7 | 4·9 | 11·3 | 25·5 | 4·0 | 22·5 | 10·17 | 0·047 |
| Sinter . | 14·6 | 0·9 | 5·8 | 2·8 | 28·6 | 4·3 | 23·9 | 11·23 | 0·052 |

As already mentioned, the sulphur in the charge should not exceed 18 p.c. and it should not be below 9 p.c. If the sulphur be too high, there is danger of the charge fritting prematurely and thus stopping the roasting process. The addition of water to the charge for the Dwight-Lloyd machine is essential. A fine dry ore is impervious to the air; moistening with about 10 p.c. of water, so that the material balls readily in the hand, results in the formation of small aggregates between which the blast passes freely.

The practice of roasting at Port Pirie, N. S. W. possesses points of interest which are worthy of consideration.³⁾ There are two classes of Broken Hill ores used, the granular ores from the jigs and tables, and the slimes from the floatation process. The composition of these is:

| | Pb | Zn | S | Fe-Mn | Al ₂ O ₃ | CaO | SiO ₂ |
|-----------------------------|----|----|------|-------|--------------------------------|-----|------------------|
| Granular Ore . | 63 | 7 | 14·5 | 4·7 | 1·5 | 1·5 | 5·0 |
| Floatation Concentrates . . | 57 | 11 | 18·0 | 4·3 | 1·0 | 1·5 | 3·5 |

¹ C. T. Rice, *Eng. Min. Journ.*, 1918, **106**, 649.

² Hofman, *Metallurgy of Lead*, p. 201.

³ G. Rigg, *Bull. Inst. Min. Met.*, 1920, **188**, 1.

These two were suitably mixed with oxidised ores, limestone and ironstone, and the mixture treated in one or other of the following ways. It was either partially roasted in a Ropp roaster and then finished off in Huntington and Heberlein pots; or it received both its preliminary and completed roastings on a Dwight-Lloyd machine. The first method yielded a satisfactory product for the blast-furnace; the second method was not so successful as the sinter lacked strength, and it was difficult to bring its sulphur-content below 5 p.c.

Since 1916, when these methods were used, experimental work has shown that the Ropp roasters can be supplanted, for the purposes of preliminary roasting, by Dwight-Lloyd machines; that ironstone can be replaced by a basic blast furnace slag,¹) and that it is advantageous for both limestone and slag-additions to be fairly finely divided, a condition attained by the use of a limestone sand, which passes the 40-mesh, and by granulating the slag in water in such a way that the particles average $\frac{1}{8}$ inch in diameter. The composition of charge and resulting sinter in the earlier and later stages of the work, as well as that of the slag formed on smelting the latter sinter in the blast-furnace, are shown in the following table:

| | 1. Old charge | 2. New charge | 3. Sinter from 1 | 4. Sinter from 2 | 5. Blast Furnace Slag from 4 |
|---------------------------------|---------------------|---------------------|------------------------|------------------------|--|
| Granular Concentrates | 49.0 | 47.0 | Pb: 44.5 Zn: 5.5 | 48.0 7.5 | — — |
| Slime Concentrates | 18.5 | 27.5 | S: 2.5 | 2.7 | — |
| Limestone | 6.0 | 7.0 | ZnO: — | — | 19.0 |
| Ironstone | 14.5 | 4.0 | FeO: 16.5 | 13.5 | 30.0 |
| Silicious Ores | 12.0 | — | MnO: 3.5 | 3.0 | 4.5 |
| Sand | — | 2.0 | CaO: 4.5 | 6.0 | 12.0 |
| Slag | — | 12.5 | SiO ₂ : 9.5 | 8.5 | 20.5 |

¹ This contained FeO = 33.5, Mn = 4.5, CaO = 14.0, ZnO = 13.5, SiO₂ = 21 p. c., along 2 p. c. of lead.

Finally, the ironstone was omitted, and the charge consisted only of concentrates, granulated slag and limestone sand (7 p.c.); this gave a sinter which was quite satisfactory for smelting in the blast furnace.

SMELTING IN THE BLAST FURNACE

All forms of shaft furnace employed in the extraction of lead have this feature in common, that the fuel and the materials to be smelted are fed in at the top of the furnace and, in their passage through the furnace, become completely liquefied. The liquid products may escape continuously through an opening at the bottom of the furnace (such a furnace being known as a *Spurofen*), or they may be allowed to accumulate in the well or crucible and be tapped off periodically. The latter method is more convenient for many reasons, one of the strongest being that it allows of more complete separation of metal from slag. Modern furnaces belong entirely to this type.

The *Slag Hearth* illustrates the older type. It is a low shaft furnace, worked with one tuyere, and was extensively used in connexion with the air-reduction process, as worked in hearths and reverberatories, for the recovery of lead from the grey slags. It is rectangular, 26 inches from back to front, 22 inches wide and 36 inches deep; the blast pipe enters at the back, 12—14 inches below the top of the furnace. It is made of cast-iron plates below the tuyere, but of fire-brick above. The bed plate slopes slightly to the open eye of the furnace. On this is placed a layer of cinders, well beaten down, the surface of which is inclined steeply upwards from the opening in front to within 2 inches of the tuyere.

The forehearth in front of the furnace has two compartments, separated by a partition reaching nearly to the bottom. The larger of these, is packed with cinders and is immediately in front of the furnace, the smaller being at the side. To start the furnace a peat fire is kindled and the blast turned on, then coke and coal added, and, when well away,

alternate charges of grey slags and coke are added at intervals, with, occasionally, ferruginous materials to aid in the reduction of lead silicate. The lead set free trickles through the cinders on the bed plate and in the forehearth, and is ladled from the smaller division of the latter. The cinders act as a filter bed, checking the flow of the viscous, black slags. The removal of the slags from the furnace is facilitated by the thrusting of a bar through the cinder bed in the furnace; the slags then flow over the cinders on the forehearth into a water-pit, where they are granulated and washed, so that shots of lead, mechanically retained by the slag, are liberated and recovered.

When used to smelt grey slags from the ore-hearth, the slag-hearth yields one thirteenth of the amount of lead produced in the ore-hearth. Four tons of grey slags can be worked off in such a furnace in 6 hours. The lead (slag-lead) is, naturally, much less pure than that produced in the ore-hearth or reverberatory. Larger blast furnaces are now usually employed in the treatment of such residues.

MODERN FURNACES

There are two types of blast furnace in general use, the round or circular, and the rectangular. The first is exemplified by the Pilz, the second by the Raschette furnace. One form of the Pilz is represented in the accompanying diagram (Fig. 16). It is 25 feet high, 4 feet 11 inches in diameter at the tuyeres, gradually widening to 6 feet 7 inches at the throat, and is supplied with 8 tuyeres.

a is the hearth bottom, composed of four courses of bricks, the lowest of common brick, resting on a circular plate $1\frac{1}{4}$ inches thick, over this are three courses of fire-bricks, all encased in boiler-plate, made in segments screwed together and further strengthened by hoops of wrought iron; *b*, channels extending through the brickwork and open at both ends to allow of the escape of moisture; *c c*, brickwork forming the inner and upper part of the hearth; *c' c'*, brickwork of the boshes; *c" c"*, brickwork

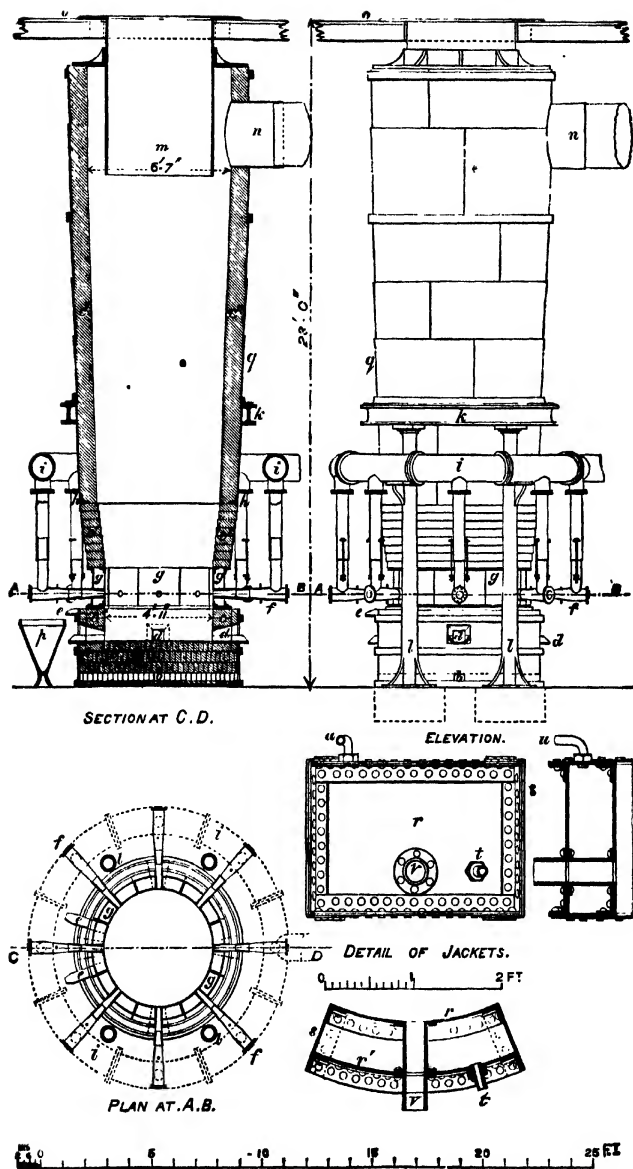


Fig. 16.—Pilz Blast Furnace.

forming the shaft; *d d*, the tap holes, of which there are four; *e e*, two slag lips, along which the slag flows into the slag pot *p*; *f f*, blast pipes, the horizontal portions of which can be moved to and from the tuyere holes; the vertical portions are supplied with a sliding screw by means of which they may be moved up and down; *g g g* are wrought-iron water-jackets made in sections, the construction of which is shown in detail in the accompanying illustrations; water-jackets may also be constructed of cast iron, each segment being provided with an aperture for the tuyere and with the necessary water-pipes; *h h*, ring of angle iron, riveted to the outer case, serving for the support of the shaft during the repairing of the lower part of the furnace; *i i*, blast main of cast iron; *k*, ring of iron supported by the four cast-iron pillars *l l*; *m*, cast-iron cylinder, flanged at the top and inserted into the mouth of the furnace, in order that the fume and waste gases may be drawn off by the pipe *n*; *o*, charging floor; *q*, outer iron casing of the furnace. The water-jackets are $\frac{1}{3}$ of an inch in thickness, and are riveted to angle iron $2\frac{3}{8}$ inches by $\frac{3}{8}$ inch; *s s* are side plates overlapping by $2\frac{3}{4}$ inches top and bottom; *t*, pipes for supplying cold water; and *u*, pipe for the outflow of cold water; *v*, tuyeres, which are $2\frac{3}{4}$ inches in diameter.

The diameter of circular furnaces varies from about 36 to 60 inches, the smaller being used for powdery, the larger for lumpy ores. The number of tuyeres varies from 8 to 24, and the blast pressure from 10 to 50 mm. of mercury. These furnaces are limited in diameter by the range of penetration of the blast, which is about 36 inches. They are chiefly used in small works, and especially in Europe. All modern ones are fitted with the Arendts' or automatic syphon tap, which will be described presently, and they are usually boshed for the better utilisation of the heat and reducing gases, and the more uniform descent of the charge.

The rectangular furnace is developed from the Raschette and, because of its great capacity, is the one almost universally used in America, where immense quantities of

suitable ore are available. The breadth of these furnaces is limited for the same reason as in the case of the circular furnaces, but the length can vary within wide limits. The dimensions of the smaller furnaces are about 42 by 84 inches, the larger ones 48 by 156 inches; an extreme size is 62 by 212 inches at the tuyere level. A view of the lower part of

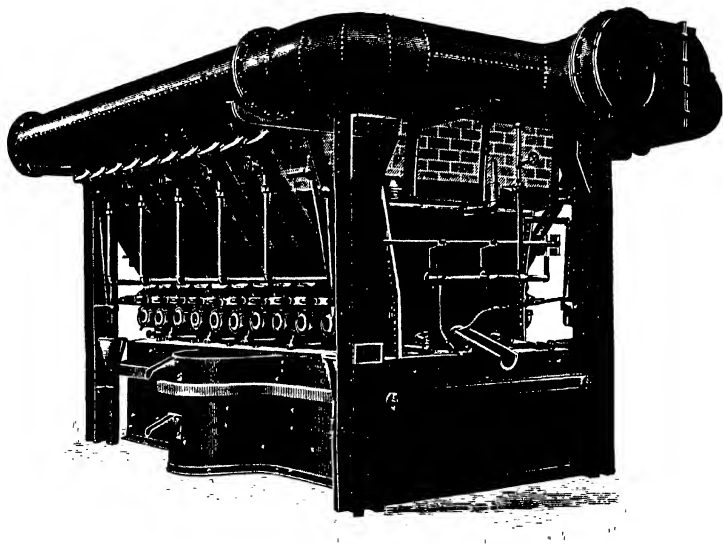


Fig 17. Rectangular Blast Furnace.

one of the larger furnaces is shown in Fig. 17. This furnace is fitted with steel water-jackets.

Fig. 18 shows a drawing of a complete modern rectangular furnace, of which the following is a brief description:

The shaft of the furnace, *A*, is made of brick and carried on a mantle ring resting on four columns. In this are four charging doors, *B*, at the feed level. The top is enclosed by a hood closed by a damper, and the fumes are drawn off into the fume chambers and bag-house by a pipe (not shown in the figure). The height of the shaft is 16—20 feet. The

zone of fusion is enclosed in water-jackets, *c*, from $3\frac{1}{2}$ —6 feet high. The use of these, and also of cold blast, prevents undue volatilisation and hinders corrosion of the hotter parts of the furnace. The blast is supplied at a pressure of about

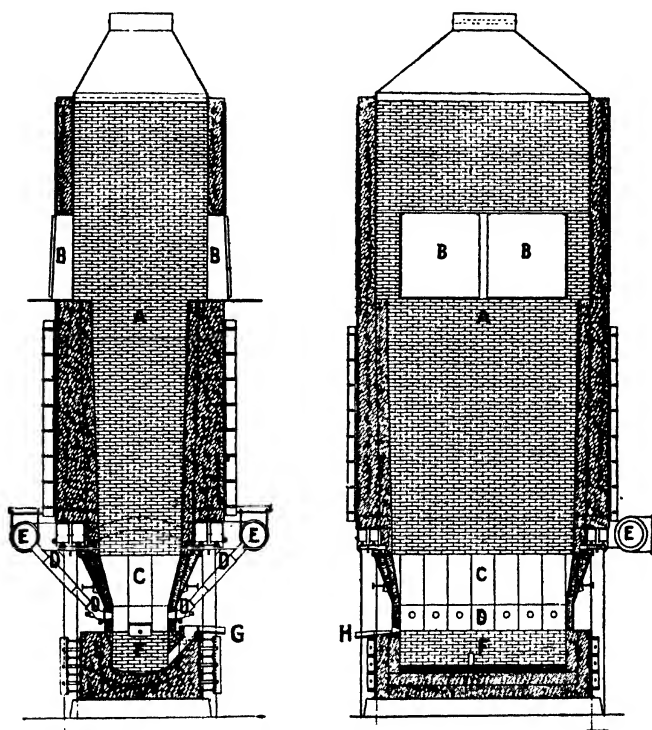


Fig. 18.—Rectangular Blast Furnace.

130 mm. of mercury and enters the furnace by 14 tuyeres, *D*, each 4 inches in diameter, which pass through the water-jackets and are distributed along the two longer sides of the furnace. As a rule, there are no tuyeres in the end jackets. The tuyeres are fed from a blast main, *E*, the connections being well seen in Fig. 17. The lower part of the furnace or crucible, *F*, is built of fire-brick and magnesia brick,

surrounded by brasque and securely held by enclosing iron walls and bed-plate. A channel 6—8 inches square leads from the crucible to the outside of furnace in the middle of one of the longer sides. This opens out into a basin and constitutes the automatic tap, *u*. The furnace is worked with the crucible full of molten lead, and the metal naturally stands at the same level in the basin as in the crucible. The lead may be run off in a continuous stream, or it may be ladled from the basin as required. The advantages of this arrangement are that the unhealthy operation of tapping is avoided, more complete separation of lead from matte and slag is effected, and the cooling which would result from emptying the crucible entirely, and the risk of the solid charge slipping down into the empty crucible are obviated. The distance of the tuyeres above the level of the lead bath is about 12 inches, and is so arranged that the heat is sufficient to keep the lead molten. Between the lead level and the tuyeres is a slag tap, *h*, from which slag and matte are continuously discharged, or tapped at intervals of 5—10 minutes. The latter method has the advantage of maintaining the fluidity of the slag; the alternate use of two slag-notches, one on each of the smaller sides, is an aid in the same direction, since it prevents cooling on one side of the furnace. Slag and matte are collected in settlers or forehearth, sometimes heated by a fire, and the matte tapped off from the slag. Such a furnace will put through 150—250 tons in 24 hours, with a coke consumption of 12 p.c. of the charge.

The charge for blast-furnace smelting consists in general of ores and mattes, roasted by the methods already described; earthy and silicious materials, either derived from the ores, or added to produce the desired slag; slags from previous operations, in amount up to 20 p.c., which are added partly to recover values present in them, and partly to facilitate the furnace-running; and coke, the usual fuel and reducing agent. Sulphide ores rich in silver are generally added direct to the blast-furnace charges, in order to obviate the loss of silver which would occur if they were roasted. The lead-

content of the charge varies considerably; 10—12 p.c. is usually regarded as a minimum, consistent with the effective action of the lead as a solvent or vehicle for the silver; 50 p.c. of lead is not uncommon, and the average may be put roughly at 20 p.c.

Great care has to be exercised in the selection of materials to produce the slag. Barren fluxes are avoided if possible, silicious silver ores and iron ores from the gossans, which usually contain some lead and precious metals, being utilised where available. The object aimed at is to produce a monosilicate, mobile when molten, and having a sp.gr. of 3.5. Analyses of slags of proved merit are given on p. 81. The blowing-in of a blast furnace has to be carefully performed, the crucible being first thoroughly dried and heated by a wood fire, and the pigs of lead melted in the crucible; as much as 30 tons may be requisite to fill the crucible. Charges of wood, charcoal and coke are followed by fusible slag, and the ore-charges are introduced gradually until the normal charge is reached. In regular working, the weighed charges are tipped on to the feed-plates, the coke is fed in even layers, and the ore is so disposed that the coarser material occupies the middle of the furnace and the fines are distributed round the sides. This method corrects the tendency of the blast to follow the walls of the furnace.

The furnace is worked with a cool throat, the temperature not exceeding 200° ; at the tuyere-level, the temperature is of the order of 1200° . The waste gases contain 5—10 p.c. of carbon monoxide, and 15—20 p.c. of carbon dioxide, the remainder being chiefly nitrogen; carbon dioxide, as might be expected, increases at the expense of carbon monoxide as the distance from the tuyeres increases, the volume-proportions $\text{CO}:\text{CO}_2$ in one particular example being, respectively, 1:1.5; 1:2.5; 1:4.5 for distances 1, 3 and 6 feet above the tuyere-level. In this matter, much depends on temperature and the composition of the charge; the former as affecting the equilibrium relations between carbon and its oxides, the latter, in that the presence of easily reducible oxides and

decomposable carbonates favours the increase of carbon dioxide. It is evident that the whole environment is a strongly reducing-one, and the sequence of reactions which occur, in the passage of the charge through the furnace, is in great measure dependent on the temperature-gradient.

At the top of the furnace, hygroscopic moisture is given off and the dried charge becomes heated up. Presently, the easily reducible oxides of lead and iron react with carbon monoxide and carbon, limestone begins to dissociate, lead sulphate is reduced to lead sulphide and possibly some reaction between these two compounds takes place, with production of lead and sulphur dioxide. About half-way down, the temperature is in the neighbourhood of 800° , and these reactions are well advanced. Others requiring higher temperature are setting in, for example, reduction of lead sulphide by iron, combination of copper with sulphur, possibly reduction of lead silicate with iron. The finely divided lead melts, the sulphide mixtures soften, and the absorption of the precious metals takes place. Finally, in the zone of fusion, occur those complex combinations and interchanges of basic and acidic oxides which result in slag-formation, the rejection of lead oxide from its union with silica and its reduction to metal, and the liquefaction of the whole material. The traversing of the liquid slag by a rain of globules of matte and metal completes the dissolution of the precious metals, and the heterogeneous mass, assembling in the crucible, is separated into layers in accordance with the specific gravities of the components. (S. G: lead = 11.5, speiss = 6, matte = 5.2, slag = 3.6.)

Of the foreign metals which accompany the ores, copper, as we have seen, forms a stable sulphide which passes into the matte. A certain amount is, however, reduced and taken up by the lead, and if the charge should contain a relatively large amount of copper (say, 10 p.c.), enough of this metal is formed to separate from the lead at a temperature much above the melting point of lead, for the eutectic alloy of lead and copper contains only 0.06 p.c. of copper, and the liquidus-

curve rises steeply from this point as the amount of copper increases. The precipitation of copper from the lead may hinder the working of the furnace and may cause great trouble by blocking the syphon-tap. Zinc is partly volatilised, and in the elemental condition may reduce some lead sulphide; some passes into the slag as silicate, zinciferous-ferrite, etc., some into the matte as sulphide; and a little may be retained by the lead. Many other metals suffer reduction and become alloyed with the lead, e.g. antimony, arsenic, bismuth; their removal from the lead will be considered later. Arsenic and antimony are partly volatilised, but they also show great disposition to unite with iron, forming thereby a speiss, which carries some copper and practically all the nickel and cobalt, when these metals happen to be present.

The products of the blast furnace are lead, speiss, matte, slag, and flue dust. The *lead*, known as work-lead or base-bullion, is almost always hard and impure, and is submitted to refining and desilverising processes, which are described later.

Speiss is formed in blast-furnace practice only when the charges are rich in arsenic or antimony and iron. It is essentially an arsenide (and antimonide) of iron, carrying some silver, a relatively large amount of gold, some lead and copper, and practically all the nickel and cobalt. Except in isolated cases, the last two metals are of no importance in blast-furnace products; a speiss rarely contains 5 p.c. of them. Some Freiberg speisses, however, have more than double this amount.

The composition of speiss is illustrated by the following table of analyses (values, per cent.) :—

| Composition of Speisses | | | | |
|-------------------------|----------|---------|-----------|----------|
| | Przibram | Laurium | Leadville | Freiberg |
| Silver | 0.037 | 0.011 | 0.008 | 0.077 |
| Iron | 61.3 | 63.8 | 60.6 | 17.8 |
| Arsenic | 18.5 | 20.7 | 31.5 | 23.4 |
| Antimony | 2.4 | — | — | 6.5 |
| Lead | 1.7 | 0.5 | 1.5 | 11.2 |
| Copper | 1.9 | 0.6 | 0.4 | 24.3 |
| Nickel and cobalt | 2.2 | — | 0.1 | 11.3 |
| Sulphur | 9.6 | 4.6 | 5.8 | 3.5 |

Speiss is desilverised by smelting in the blast furnace; copper passes into the matte, and nickel and cobalt are concentrated in the new speiss. Thus, a raw speiss containing 6 p.c. of nickel and cobalt and 0.16 p.c. of silver yielded on smelting a new speiss containing 16 p.c. of nickel and cobalt and only 0.05 p.c. of silver. Rich speisses may be roasted with pyrites, when the arsenic is volatilised as sulphide, and the residues smelted, with silicious additions, in the blast furnace.

The *matte* is tapped with the slag into a settler or fore-hearth, where separation takes place and from which the lower layer of matte is tapped into a receiver. Sometimes the separation is effected in a reverberatory furnace. Mattes usually contain 10—20 p.c. of lead, along with some copper, the composition varying within wide limits, as may be seen from the following analyses:—

| Composition of Mattes | | | | |
|-----------------------|------|----------|---------|-------|
| | Oker | Przibram | Laurium | Dapto |
| Iron | 30.5 | 41.3 | 50.8 | 46.6 |
| Lead | 5.1 | 11.2 | 7.7 | 15.4 |
| Copper | 16.8 | 1.5 | 1.8 | 3.9 |
| Zinc | 16.3 | 11.5 | 7.6 | 6.4 |
| Sulphur | 16.4 | 22.2 | 21.8 | 25.0 |

Mattes always carry some silver and gold, but silver is relatively more soluble in them than gold. They are roasted and added to blast-furnace charges, whereby the iron becomes available for slagging and reduction purposes, and a new matte, enriched in copper, is formed. When the copper-content rises to 10 p.c., the mattes are roasted down to 3—4 p.c. of sulphur and then smelted with liquation-residues and silicious copper ores. After enrichment to 30—40 p.c. of copper, they are usually sold to the copper smelters and treated for copper by the converter, or some other, process.

Slags have already been considered with respect to their composition and fitness for the smooth running of furnace

work. The clean separation of slag from matte (and speiss) is of great importance, and depends largely on their relative fluidities and specific gravities. Matte is dissolved to some extent by slag, acidic slags dissolving less than basic, and calcareous less than ferruginous slags.

Lead, also, is soluble to a slight extent in its own slags. Analyses of slags from the blast furnace are given in the table below.

| Composition of Slags | | | | | | |
|--|----------|----------|----------|-----------|-------|------------|
| | Braubach | Freiberg | Przibram | Pertusola | Trail | Herculanum |
| (Fe, Mn)O . . | 43·8 | 45·3 | 30·9 | 32·9 | 29·0 | 36·7 |
| (Ca, Mg)O . . | 17·1 | 5·3 | 15·8 | 21·5 | 20·5 | 18·4 |
| ZnO | 4·3 | 14·8 | 4·0 | 12·9 | 10·0 | 5·6 |
| Al ₂ O ₃ | 2·3 | 4·4 | 7·8 | 3·1 | 6·5 | 3·7 |
| SiO ₂ | 27·8 | 24·0 | 37·5 | 26·7 | 32·0 | 32·3 |
| S | 2·7 | 4·4 | 0·9 | 1·0 | — | — |
| PbO | 0·3 | 2·9 | 0·5 | 1·1 | 1·6 | 1·5 |
| CuO | 0·1 | 0·8 | — | — | — | — |
| Ag (ozs.) . . | — | — | 0·3 | 2·7 | 0·75 | — |

Flue dust.—The methods for the collection and treatment of this will be described later.

The loss of lead in the blast furnace is variable, 7 p.c. on the dry assay being considered satisfactory. The loss of silver is very small by this method, whereas in the roasting-and-reaction process the average loss is about 1·5 p.c.

The basis of the modern American and Australian practice of lead-smelting is blast roasting of ores, by the Huntington-Heberlein or Dwight-Lloyd methods, either singly or combined. This is sometimes preceded by roasting in cylinders or reverberatories and is followed by smelting of the roasted ore, with the addition of suitable fluxes, in rectangular, water-jacketed furnaces of large capacity.

Interesting information concerning the working of the modern blast furnace is contained in the following table.¹⁾

¹ Hofmann, *Metallurgy of Lead*, p. 218.

In all cases, the furnaces worked without the production of speiss, and the coke-consumption varied from 12 to 14 p.c. of the weight of the charge.

| | Midvale, Utah | Salida, Colorado | Hercula- neum, Missouri | Toole, Utah | Trail, Brit. Columbia | Cockle Creek, New South Wales | North- port, Washing- ton |
|--|------------------|---------------------|-------------------------------|----------------|-----------------------------|---|------------------------------------|
| Lead, p.c. of charge . . | 11—18 | 10 | 38 | 16·5 | 15—22 | 33 | 25 |
| Copper, p.c. of charge . | 0·7—1·0 | 1·0 | 1·0 | 0·8 | 0·4 | none | small |
| Sulphur, p.c. of charge . | 2·5—3·8 | 4·0 | 4·5 | 3·1 | 3·5 | 2 | 4 |
| Work lead: ozs. per ton of silver & gold . . . | 80—160 | 170 | 26—3·2 | 72·9 | 120 | 80 | 80 |
| Matte: p.c. of charge . . | 10 | 10·4 | 13·8 | 6·5 | 7 | none | 9 |
| Matte: lead, p.c. . . . | 10—18 | 14·5 | 13·0 | 12·3 | 18 | — | 16 |
| Matte: copper, p.c. . . . | 6—12 | 12·3 | 2·5 | 11·0 | 8 | — | 3 |
| Matte: ozs. per ton of silver and gold . . . | 30—50 | 53·5 | — | 17·7 | 35 | — | 30 |

Further details will be illustrated in the following examples.

EXAMPLES OF BLAST FURNACE SMELTING

Smelting at Clausthal and Lautenthal in the Lower Harz is of interest, in that it is a survival of the old method whereby sulphide ores were reduced with metallic iron. The composition of the dressed ores varies within considerable limits, the chief constituents being lead 50·7—73·6, sulphur 8·5—14·2,

silica 5.9—32.4 p.c.; they also contain a small amount of copper, 0.6 p.c. and a notable quantity of silver, 0.05—0.185 p.c. ¹⁾

Formerly, these ores were smelted with fuel and metallic iron. The iron was replaced later by ferruginous materials, reducible to iron in the blast furnace; such were the residues (Oker slags) left in the wet process for the extraction of copper from cupriferrous pyrites, which contained 70 p.c. oxide of iron, with 1—2 p.c. of copper and 17—21 p.c. of silica. When these were no longer obtainable, burnt pyrites, roasted matte, haematite, hammer scale and tap cinder were used as substitutes. These materials are smelted in circular furnaces at low blast pressure.

The following table gives the composition of the charges, at different periods, in parts by weight:

| | 1. | 2. | 3. |
|--------------------------|----|----|----|
| Sulphide ores | 50 | 50 | 50 |
| Roasted lead matte . . . | 24 | 30 | 30 |
| Ore slags | 27 | 30 | 40 |
| Matte slags | 21 | 25 | 25 |
| Oker slags | 30 | — | — |
| Mill cinder | — | 20 | 10 |
| Roll scale | — | 5 | — |
| Limestone | — | 9 | 8 |

At Lautenthal, where the work-lead is desilverised, the blast furnace charges contain, in addition to the above constituents, litharge and cupellation hearths. The consumption of coke is 13 p.c. on the whole charge, or 40 p.c. on the ore. The slag from the ore smelting flows away continuously; it is highly ferruginous, the chief constituents being: $\text{FeO} = 40$, $\text{CaO} = 4$, $\text{ZnO} = 8$, $\text{Al}_2\text{O}_3 = 7$, $\text{SiO}_2 = 31$ p.c. Matte and metal are tapped together, the former allowed to set and the solid cake lifted from the surface of the lead. The amount of matte produced is very large, exceeding somewhat the weight of

¹ Kerl, *Grundriß der Metallhüttenkunde*, p. 60.

work-lead. It is roasted in heaps or kilns and the roasted product smelted in small furnaces with ore-slag and coke. This yields a small amount of highly argentiferous lead and a new matte enriched in copper. This is roasted and smelted again in a similar manner several times; no lead is obtained after the second matte smelting, but only an impure black copper and a fresh matte. The composition of the mattes produced in these operations is shown in the annexed table.¹⁾

| | First (ore) Matte | Second Matte | Third Matte | Fourth Matte | Fifth Matte | Sixth Matte |
|--------------|-------------------------|-----------------|----------------|-----------------|----------------|----------------|
| Lead . . . | 12.4 | 8.0 | 13.0 | 9.0 | 6.3 | 3.9 |
| Copper . . . | 3.5 | 12.3 | 35.7 | 42.3 | 58.1 | 59.9 |
| Iron . . . | 48.7 | 45.6 | 21.9 | 19.0 | 11.0 | 12.2 |
| Zinc . . . | 4.3 | 3.4 | 2.2 | 1.6 | 1.0 | 0.7 |
| Silver . . . | 0.035 | 0.035 | 0.08 | 0.075 | 0.06 | 0.035 |
| Sulphur . . | 25.6 | 21.8 | 19.5 | 17.9 | 20.1 | 20.8 |

With the successive roastings and smeltings, the proportion of coarse copper increases relatively to that of matte and the latter varies but little in composition, the enrichment in copper not exceeding 60 p.c. of that metal: the matte slags are highly ferruginous, containing about 65 p.c. of ferrous oxide, 18 p.c. of silica and a few per cents each of lime, zinc oxide and alumina.

Smelting at Binsfeld.—The ores containing 70 p.c. of lead are mixed with limestone and sand and roasted in the Dwight-Lloyd machine. The roasted material contains 58 p.c. of lead. 1000 parts of this are mixed with 180 of ferruginous slag, 50 of spathic iron ore, 400 of slags from the same operation, and 100 of various lead-bearing materials. This is then smelted in rectangular blast-furnaces, 40 by 148 inches at the tuyeres. Each furnace has 19 tuyeres and smelts 250 tons of the charge in 24 hours, yielding 70—80 tons of lead. The slags carry 2 p.c. of lead.

¹ Collins, *op. cit.*, p. 298; Schnabel, *op. cit.* p. 542.

Smelting at Freiberg.— The ores are partly native and partly foreign, the latter being chiefly Canadian. They are classified according to their composition, and their treatment depends upon this. Ores containing over 25 p.c. of sulphur are roasted at the sulphuric acid works, the lump ore in kilns and muffles down to 3—6 p.c. of sulphur, the fines in *Schüttöfen* down to 8 p.c. of sulphur. Galena, containing over 30 p.c. of lead, and leady ores with 10—30 p.c. lead are mixed with roasted fines, and other materials, and roasted either in long-bedded calciners, or in Huntington and Heberlein pots.

The reverberatories are 54 feet 6 inches long, and 14 feet wide; they put through 12 tons in 24 hours, the separate charges being 1·5 tons. The charges consist of 2·1 parts of galena and leady ores, 1·2 of dry silicious ores (containing less than 10 p.c. each of lead and sulphur), and 2 parts of roasted fines, and they are divided into rich ores, carrying 0·5—0·7 p.c. of silver, and poor ores, carrying 0·1—0·3 p.c. of silver. The composition before and after roasting is given in the following table—

| | Lead (p.c.) | Zinc (p.c.) | Copper (p.c.) | Sulphur (p.c.) | Silica (p.c.) | Silver (p.c.) |
|-------------------------|----------------|----------------|------------------|-------------------|------------------|------------------|
| Rich { Before roasting | 24 | — | 0·5 | 12·5 | 22 | 0·48 |
| ores { After roasting . | 26 | — | 1·0 | 4·3 | 24 | 0·64 |
| Poor { Before roasting | 30 | 7 | — | 8·4 | 22 | 0·09 |
| ores { After roasting . | 33 | 11 | — | 2·6 | 23 | 0·11 |

The converters for blast roasting hold 2—3 tons. Roasted fines are added to the ores instead of limestone, and the charge for pre-roasting is made up of 2·4 parts of galena, 0·9 of dry ores, and 1·5 of roasted fines, and averages 36 p.c. of lead and 14 p.c. of sulphur. This is roasted in rotating furnaces, the sulphur being reduced thereby to 10 p.c. and the roasted product mixed with 50 p.c. of the ore-mixture and again roasted in Huntington and Heberlein converters; in this way the sulphur is brought down to 3 p.c.

For smelting, circular furnaces of the Pilz type are used. The largest of these are 36 feet high, 6 feet 6 inches diameter

at the tuyeres, and 8 feet at the throat; there are 20 tuyeres, and the blast pressure is 10—15 mm. of mercury. The charge consists of the roasted ore, mixed with about two-thirds of its weight of slag from a previous operation, 2 p.c. of burnt pyrites, and small amounts of dry ores. The consumption of fuel (coke) is about 15 p.c. of the charge. The work-lead contains 0.5—2 p.c. of silver; the matte-fall is about 10 p.c., and the matte contains 20—25 p.c. lead, 6—10 p.c. of copper, and 0.1—0.25 p.c. of silver; the slags carry 4—6 p.c. of lead and 0.015 p.c. of silver. It is characteristic of Freiberg practice that no attempt is made to produce clean slags. They are re-smelted with roasted matte and leady additions, the latter being added in such quantity as to yield sufficient lead to keep the new matte poor in precious metals. After one or two slag-smeltings, a clean slag is produced, which can be thrown away. A typical analysis of such a slag shows: lead, 1—2; silver, 0.001; copper, 0.3; zinc, 9—12; ferrous oxide, 50; and silica, 30 p.c.

Smelting at Laurium.—The mines in this district were worked by the Greeks as early as the sixth century B.C. and the dumps and slags have received treatment several times since then. When operations were restarted in recent times, the old slags, which contained $PbO = 8—15$ p.c., were smelted with limestone and ironstone in slag-hearths.

Roasting of sulphide ores in Oxland furnaces, followed by blast-roasting in pots, was initiated in 1906, and the roasted ores were smelted in circular blast-furnaces, with a capacity of 25 tons a day. Shortly afterwards, large, rectangular furnaces were installed, 28×160 inches at the tuyeres, with 10 tuyeres on each of the longer sides. The crucible lining is of refractory brick, composed of chromite (1 part) and calcined magnesite (3 parts), this mixture being found suitable for withstanding the corrosive action of the speiss produced in the smelting. The charge is self-fluxing and averages 11 p.c. of lead, of which 91 p.c. is recovered as work-lead, which contains 97.4 p.c. of lead and 0.15 p.c. of silver. The furnace-capacity is 250—300 tons of ore in 24 hours and, in addition to the

work-lead, 3—5 tons of matte and 7—9 tons of speiss are produced. The slags contain: (Fe,Mn)O=26; (Ca,Mg)O=17; SiO₂=25 p.c. and they carry 0.8 p.c. of lead and the same amount of sulphur. The composition of the matte and speiss is (p.c.)¹:—

| | Fe | Cu | Pb | Zn | As | Ag | S |
|--------------|------|-----|-----|-----|------|-------|------|
| Matte . . . | 50.8 | 1.8 | 7.7 | 7.6 | 0.4 | 0.028 | 21.8 |
| Speiss . . . | 63.8 | 0.6 | 0.5 | 1.7 | 20.7 | 0.011 | 4.6 |

Smelting at Trail (British Columbia).—The chief ores are sulphide, which are mixed with lead matte and limestone, so as to have the following composition:—

| | |
|------------------------|----------------|
| Lead | 40—44 p.c. |
| Ferric oxide | 10—13 „ |
| Limestone | 7—10 „ |
| Silica | 8—11 „ |
| Sulphur | 14—17 „ |
| Zinc Oxide | less than 10 „ |

This mixture is roasted in revolving hearths, so as to bring the sulphur down to 8—9 p.c. It is then further desulphurised and sintered by blast-roasting in Huntington-Heberlein pots, of which there are 24, each 8 feet 8 inches in diameter. The charge for the blast-furnace is made up of 85 parts of the sintered material, 2.5 of oxidised lead ores and silicious gold and silver ores, and 12.5 of coke, the average lead content being 40 p.c. and the sulphur below 4 p.c. This is smelted in rectangular blast furnaces, 45 by 160 inches as the tuyeres, the blast pressure being 32 ozs. and the height of the column above the tuyeres 17½ feet. The output of work-lead per day from each furnace is 75 tons, and its composition is shown in the following table:—

| | |
|------------------|-----------|
| Lead | 98.5 p.c. |
| Copper | 0.22 „ |

¹ Collins, op. cit., p. 303.

| | |
|--------------------|------------|
| Zinc | 0.098 p.c. |
| Bismuth | 0.013 „ |
| Antimony | 0.32 „ |
| Arsenic | 0.28 „ |

The base bullion carries 100 ozs. of silver and 0.1 oz. of gold per ton. It is cast into anode plates and refined electrolytically by the Betts' process.

The slags carry 1 p.c. of lead and 0.4 oz. silver per ton, and have the following percentage composition: (Fe,Mn)O = 24—30; (Ca,Mg)O = 18—20; ZnO = 7—12; Al₂O₃ = 8—16; SiO₂ = 31—33.¹

Smelting at Broken Hill.—The concentrates treated by the Associated Smelters' Proprietary Co. contain 60 p.c. of lead, 15 p.c. of sulphur, and 20—25 ozs. per ton of silver. Two processes for roasting the concentrates are used.

1. The ore is mixed with ground limestone and ironstone, moistened and charged on to the Dwight-Lloyd machine. Thence it is conveyed to the rolls, ground and moistened and roasted again in a similar manner.

2. The ore-mixture, as above, is roasted in a Ropp furnace, 156 feet long and 14 feet wide. The roasted material is charged hot into Huntington and Heberlein converters of 10 tons capacity, and air blown through at 1½ lbs. pressure. The sintered mass is tipped and broken up and is ready for smelting. The output of 3 Ropp roasters, 20 converters, and 9 Dwight-Lloyd machines is 500—550 tons a day.

The roasted ore is smelted in rectangular blast furnaces 17 feet long, 4 feet 6 inches wide, and 25 feet high, over all. Three of these are used, and they are capable of putting through 1200 tons of total charge a day. The charge consists of roasted and sintered ore, ironstone, limestone, slags from a former smelting, and coke. The daily output of base bullion is 400 tons, containing 40—50 ozs. per ton of silver, and, in addition, copper (0.5 p.c.), antimony, and arsenic. The slags are clean and amount to 750 tons a day; 20—25 tons of fume

¹ J. M. Turnbull, *Mines and Minerals*, 1910, 31, 121.

are condensed every week by bag-filtration, and this is collected and re-smelted to recover lead.

Smelting at Cockle Creek, N.S.W.: The ores, chiefly from Broken Hill Central Mine, are roasted, when rich enough in sulphur, in circular, revolving, gas-fired hearths (Godfrey furnaces), 21 feet in diameter. The charge averages $Pb = 50$ p.c., $S = 15$ p.c. and the sulphur is reduced to 9.5 p.c. There are 10 such furnaces, each of which puts through 30 tons in 24 hours; the ore is discharged into brick-lined boxes around the periphery and is transferred hot from these to the Huntington-Heberlein pots for further desulphurisation. There are 24 of these pots, each holding 10 tons and worked by a blast pressure of 10—12 ozs. When in operation, they are covered with a hood, and the gases are drawn into a pipe, whence they are led into sulphuric acid chambers; the gases poor in oxides of sulphur can be by-passed into the open air. After 6—8 hours blowing, the converter is turned and the fritted mass tipped out, cooled with water and sledged down to 6 inch size. This material constitutes 75 p.c. of the blast-furnace charge.

There are three blast-furnaces, the largest 11 feet 6 inches by 5 feet at the tuyeres, and 36 feet high from the tapping to the feed floor with 13 tuyeres, 3 inches in diameter. This holds 100 tons when full and puts through daily 300 tons of charge, yielding 100 tons of work-lead. The matte is crushed and added to the blast-roasting charges; slag-shells from the slag pots are added to smelting charges.¹⁾

CHAPTER VI.

THE SOFTENING & DESILVERISING OF LEAD

SOFTENING OF HARD LEAD

The lead obtained by smelting contains variable quantities of the precious metals. Leads from Missouri and Wisconsin, for example, are almost free from them, whereas the silver

¹ *Eng. Min. Journ.*, 1919, 108, 394; *Min. Mag.*, 1919, 372.

and gold in some bullion-leads is worth more than the lead which contains them. In addition to the precious metals, work-lead contains a number of base metals, most of which make the lead hard, unfit it for commercial purposes, and render the profitable extraction of silver an impossibility. The following analyses of work-lead illustrate the nature and range of the chief impurities:—

| Origin | Per cent | | | | | | Ozs. per ton | |
|--|----------|-------|------|------|-------|-------|--------------|------|
| | Pb | Cu | Sb | As | Bi | S | Ag | Au |
| English (Weardale) . | 99.87 | 0.015 | 0.05 | 0.01 | 0.001 | 0.015 | 7 | — |
| German (Freiberg) . | 96.67 | 0.94 | 0.82 | 0.28 | 0.066 | 0.20 | 180 | — |
| Spanish (Magarron) . | 99.20 | 0.22 | 0.20 | 0.15 | 0.004 | 0.11 | 9 | 0.06 |
| „ (Orcellitana) . | 98.92 | 0.15 | 0.40 | 0.21 | 0.005 | 0.10 | 45 | — |
| Greek (Laurium) . | 98.27 | 0.75 | 0.55 | 0.10 | 0.010 | 0.08 | 45 | 0.07 |
| Turkish (Balıa Ka- raidini) | 98.36 | 0.35 | 0.50 | 0.23 | 0.058 | 0.22 | 62 | 0.17 |
| American (Tomb- stone, Arizona) . | 98.50 | 0.22 | 0.32 | 0.28 | 0.013 | — | 100 | 0.10 |
| Mexican (Torreon) . | 95.40 | 0.08 | 1.80 | 1.30 | 0.050 | 0.35 | 300 | 1.50 |
| „ (Magapil) . | 95.72 | 0.09 | 2.50 | 0.90 | 0.030 | 0.32 | 105 | 0.42 |

There are also, on occasion, small quantities of tin, zinc, iron, nickel, and cobalt present in work-lead. Almost all of these impurities have a deleterious effect on the desilverisation process, arsenic being one of the worst in that respect, and their removal is consequently an operation of great importance. Many of them are more easily oxidised than lead, and can thus be eliminated by oxidation of the molten metal, the oxides forming a dross on the surface. Bismuth and copper are not so easily oxidised as lead. Copper, however, being but sparingly soluble in lead, near the melting temperature of the latter, can be in part removed by liquation. The elimination of bismuth is a very difficult matter; fortunately, its effect on the properties of lead is not very harmful for most purposes, when present in moderate amounts. In the Pattinson process (*q.v.*) it is retained in the rich alloy and passes eventually into the litharge when the rich alloy is cupelled; it can be com-

pletely removed only by the electrolytic method of refining. Missouri leads are singularly free from bismuth; a single liquation of the crude lead is usually sufficient to yield a product suitable for all purposes except corroding, that is, conversion into white lead. In general, the purification of work-lead is brought about by drossing the oxidisable impurities, a process known as 'improving' or 'softening.' When the work-lead contains much copper, drossing is preceded by liquation.

Liquation is carried out at a low temperature, on a hearth with sloping bottom, the lead draining away into kettles, leaving the liquation-residues rich in copper. In Freiberg, the furnaces are 5 feet 8 inches by 5 feet 6 inches; the liquation residues contain all the sulphur, 96 p.c. of the nickel and cobalt, 93 p.c. of the copper, and 25 p.c. of the arsenic which were present in the base bullion. The analysis of these residues show: lead, 62.4 p.c.; copper, 17.97; arsenic, 2.32; antimony, 0.98; tin, 0.04; nickel and cobalt, 1.09. They are treated by smelting either in small cupolas with low-grade matte, or in blast furnaces with galena, the copper being recovered in the matte.

The *improving* or *softening* is effected in a reverberatory furnace. A simple type, which was at one time the standard pattern, consists of a cast-iron pan, which forms the lead bath. It is about 2 inches in thickness, 10 feet long, 5 feet 6 inches wide, and 10 inches in depth. All the angles of the casting are carefully rounded to prevent breakage by expansion or contraction, and the softened lead is drawn off by a hole bored in the bottom, near the outer edge, which is stopped by a well-fitting iron plug held in its place by a weighted lever.

This type of furnace is usually made to hold from 8 to 12 tons of molten lead. The fireplace is about 20 inches wide, and has a length equal to the width of the cast-iron pan, from which it is separated by a bridge 2 feet wide. The height of the furnace above the pan at the bridge end is 16 inches, and at the other end 8 inches.

The charge is introduced either in the form of pigs, or is

first melted in an iron pot, set in brickwork, at the side of the furnace, and subsequently ladled into a sheet-iron gutter, by which it is conveyed to the furnace. This kind of furnace is easy to erect, but is too small for present-day conditions, where large throughput is required. Modern furnaces are much larger, and have the lead bath built of brick usually set in a wrought-iron pan. They are supported on rails and held up by buckstays. The bottom of the furnace is built of a layer of brasque, and the hearth is rectangular; the size varies according to requirements and the sides are sometimes water-jacketed; the hearth slopes to the tap-hole, which is rammed with clay or furnished with a tapping plug. There are usually two working doors on either side of the furnace, through which the lead is charged, and through which the scums are withdrawn. The size of the fire-grate varies considerably. Some practical men prefer small ones, which, though lengthening the period of drossing, reduce the loss by volatilisation. The capacity of these furnaces is 50 to 300 tons of lead.

In the softening process, the molten lead is submitted to the action of heated air, whereby the easily oxidisable impurities are converted into oxides, which, floating on the surface of the bath, are removed by a perforated skimmer; in this way a fresh surface is constantly exposed to oxidation. The progress of the operation is judged by taking a sample in a ladle and casting it in an iron mould; when the drossing is complete the surface presents a peculiar, flaky crystalline appearance. The improved or softened lead is then tapped into an iron pot, from which it is ladled into the pig moulds, or is run from the furnace, by a movable iron gutter, into a series of pig moulds, placed in a semi-circle in front of the furnace. It is then ready for delivery to the desilverising plant.

When the work-lead contains tin, this is the first metal to be oxidised, and the oxide separates as a powder. This is followed by the arsenic and then the antimony dross, each of which is liquid; the metals are present as arsenate and antimonate of lead. These stages are, however, not clearly

defined, but merge into one another. The complete removal of these impurities is facilitated by the addition of litharge to the bath, and becomes apparent by the change in appearance from the dark, oily dross of lead antimonate, to the yellow scum of litharge.

The course of the dressing is illustrated by the following partial analyses of Freiberg drosses:—

| | First tin dross (powder) | Second tin dross (liquid) | Arsenic dross | Antimony dross |
|-------------------------------|--------------------------------|---------------------------------|------------------|-------------------|
| SnO_2 . . . | 14.7 | 12.2 | 0.6 | 0.3 |
| As_2O_3 . . . | 0.9 | 11.2 | 16.2 | 4.0 |
| Sb_2O_3 . . . | 12.5 | 18.6 | 8.5 | 32.2 |

The duration of the process at Freiberg is 2—14 days, and the yield of refined lead 75—85 p.c.

Drosses from the improving furnace are melted in a reverberatory furnace with a little coal, whereby some lead is liberated and this desilverises the dross; the residue is smelted in blast furnaces and yields an impure antimonial lead. Much of the arsenic is volatilised in the blast furnace.

DESILVERISATION OF SOFT BULLION LEAD

The methods used in the extraction of the silver from soft or improved lead vary according to the silver-content of the lead. Low-grade leads are submitted to a concentration-process and the rich alloy thus obtained is cupelled. The concentration is effected by the Pattinson process, or some modification of it. High-grade leads are cupelled; if fairly rich in silver, they are melted, stirred with zinc, and the alloy of zinc, lead, and silver which separates on cooling is worked for silver. This is Parkes' process.

THE PATTINSON PROCESS

The concentration of silver in poor silver-bearing lead is founded on an observation made by Hugh Lee Pattinson, of

Newcastle-upon-Tyne, that the crystals, which first separate from a molten alloy of silver and lead, are poorer in silver than the residual alloy. This discovery was made the basis of a patent by Pattinson, for 'An improved method of separating silver from lead,' the date of which is October 28, 1833.

In this year, large scale operations were begun in iron pots holding 4—5 tons of lead. The crystals formed on cooling a lead containing 8 ozs. per ton of silver, carried at first only 1—2 ozs. which rose, a little later, to 2—3 ozs.; after removing three-quarters of the charge from the crystallising pot, the residual alloy contained 20 ozs. of silver per ton. Liquefaction of the crystals led to considerable enrichment in silver in the earlier runnings, a 12 oz. lead yielding one fifth of its weight of 50 oz., lead, the remainder carrying only three quarters of an ounce of silver per ton. This method was abandoned in favour of repeated crystallisation, for it was found that the drossing of the lead was a serious disadvantage, and the maintenance of a suitable temperature for liquation presented great difficulties.

It is evident that Pattinson had a fairly shrewd idea of the principles involved in his famous process, for he says of the liquation-method: "The separation is effected by the difference in fusibility between pure lead and lead containing silver, aided no doubt, by the tendency of pure lead, in that state of semi-fluidity [in the sweating furnace] to assume a crystalline form." His explanation of the phenomena of crystallisation of argentiferous lead is given in these words: "The most simple view of the matter is, undoubtedly, that it is an instance of true crystallisation, in which the homogeneous particles of lead are drawn together in virtue of their molecular attraction, to the exclusion of the foreign body, silver."¹ The complete explanation of the process was only possible at a much later date, as a result of the intensive study of the properties of solutions.

The behaviour of a molten silver-lead alloy on cooling is

¹ H. L. Pattinson, *Brit. Ass. Report.*, 1838. 30.

similar to that of a salt solution. The freezing point is lowered proportionately to the amount of silver dissolved, pure solvent crystallises out and the mother-liquors become enriched in the solute with the progress of crystallisation, until finally a stage is reached when the residual liquor freezes as a whole at a constant temperature. This is the eutectic point. The alloy then has the lowest melting point and further concentration of any constituent by the process of crystallisation is impossible, since the composition of the eutectic liquid and the crystals derived from it is the same.

The melting point of pure lead is $328^{\circ}\text{C}.$; the eutectic mixture of lead and silver melts at $303^{\circ}\text{C}.$ and contains 2.25 p.c. of silver (about 900 ozs. per ton). In practice, this limit of concentration is never reached, the enrichment not exceeding 1.75 p.c. of silver, *i.e.* 650 ozs. per ton. Further, it is impossible to separate completely the crystals of pure lead from the freezing alloy, since they always carry with them, mechanically, some of the silver-bearing mother-liquors. To obtain, therefore, effective concentration of silver, it is necessary to repeat the operations several times, so that the process becomes, in fact, one of fractional crystallisation.

These considerations naturally apply only to pure silver-lead alloys. The presence of foreign metals disturbs the crystallisation and concentration processes in various ways.

Copper, arsenic, and antimony have the curious effect of making the crystals of lead small, so that they are difficult to drain and thus carry silver with the retained mother-liquor. Zinc, if present, acts as in Parkes' process, carrying the silver into the first fractions and thus rendering the process inoperative. Bismuth and nickel remain almost entirely (copper to some extent) in the mother-liquors and so pass on to the cupellation process with the rich alloy.

The equilibrium-diagram for the alloys of silver and lead is given in Fig. 19. It will be observed that solid solutions are not formed¹) and that the eutectic point lies near to the

¹ K. Friedrich, *Metallurgie*, 1906, 3. 396; Haycock and Neville, *Phil. Trans.*, 1897, 189A, 25.

lead end of the curve. The curve AO represents the conditions of temperature and concentration, under which pure lead separates from the argentiferous lead, and is the one of particular interest in connexion with the Pattinson process. O is the eutectic point, at which the alloy has the lowest melting temperature, and OB the curve representing the

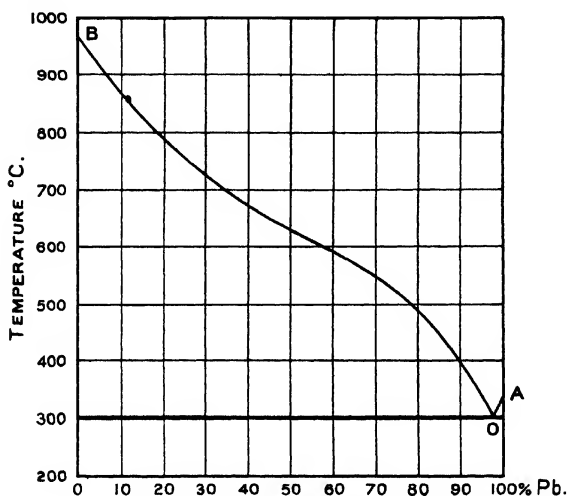


Fig. 19.—Equilibrium-Diagram of Alloys of Silver and Lead.

separation of silver from hypereutectic alloys; the latter do not concern us here.

The operation of pattinsonising, at it is called, is conducted in large cast-iron pans or pots, 5-7 feet in diameter, 3 feet deep, $1\frac{1}{4}$ -3 inches thick at the bottom and 1-2 inches thick at the top. These hold about 12 tons of lead, extreme capacities being 6 and 18 tons. Round the top of the pan is a projecting rim, which rests on an iron ring set in masonry; this serves as a means of support for the pan. Each pan is fired separately, the hot gases passing round the under surface by means of a circular flue. A line of pans, usually 9 to 12 in number, placed in line, constitutes a battery; the end

one is smaller than the others (about two thirds the size) and is called the market pot; the desilverised lead passes to this pot and is ladled or run from it into the pig moulds. Small-sized lead pots, also separately heated, placed by the side of the larger pots, are used for the purpose of heating and cleaning the ladles. These are perforated and made of half inch iron, and when worked by hand are 16 inches diameter and 5 inches deep, the holes being $\frac{1}{2}$ inch in diameter and the handle about 10 feet long. Larger ladles, 20 inches in diameter, 6 inches deep and perforated with three-quarter inch holes are operated by means of a crane. A chisel-pointed bar or slice is used for stirring the lead and loosening crusts from the side of the pot.

The method of setting a battery of pots, along with details of the arrangement of flues is shown in Fig. 20.

For the working of the process, pigs of the argentiferous lead are charged into one of the pots, between the rich pot at one end of the battery and the poor or market pot at the other end, the position selected depending on the silver-content of the lead. A rich work-lead is placed nearer the rich pot, so that the enriched alloy has not far to travel, while, on the other hand, the crystallisation-process has to be repeated many times, in order to obtain a market lead, so that the crystal-crops, poor in silver, have to be subjected to many operations before the market-pot is reached.

After the lead is melted down, the dross is removed with a ladle and the fire then drawn; water is sprinkled on the surface of the metal to promote cooling and the cakes of solid metal which are formed are broken up with the slice and stirred into the liquid. The stirring is continued throughout the period of crystallising, so that the crystals are kept small. As solid lead is specifically heavier than liquid lead, the crystals sink to the bottom of the pan, and when it is judged that a sufficient quantity has been formed, they are moved by means of the perforated ladle. This is plunged to the somewhat pasty mass of metal, gradually raised above the surface, the edge of the pot serving as a fulcrum, brought

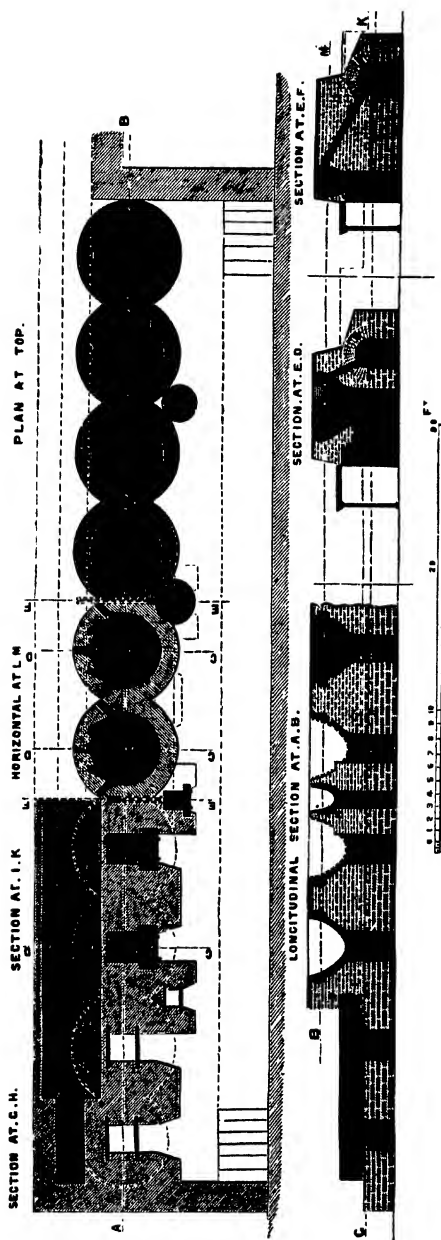


Fig. 20.—Pattinson Desilverising Plant.

into a tilting position and the liquor allowed to drain from the crystals; the crystals are then transferred to the neighbouring pot and the operation repeated until two-thirds of the metal has been removed. The residual, rich bottoms are then ladled to the next pot on the other side.

Thus, in one operation, a charge, say, of 20 oz. lead is resolved into two parts; two-thirds of it, containing about 11 ozs. of silver per ton has been moved one stage towards the market pot, and the remaining third, with 40 ozs. of silver per ton, has similarly been transferred towards the rich pot. The full charge in the new pots is now made up, by the addition of lead having the same silver-content, or by the pattinsonising of another 20 oz. charge in the original pot. The poorer lead and enriched bottoms are then subjected to the same process and by systematically passing the crystals in one direction and the rich alloy in another, a lead is obtained in the market pot, containing only about 10 dwts. of silver per ton, whereas the rich alloy at the other end of the battery may contain 600—700 ozs. per ton. Further concentration than this is not practicable.

In this system of thirds, as it is termed, each operation results in the doubling of the silver content of the rich alloy, with leads ranging downwards from 50—60 ozs. of silver per ton. The low system, or system of eights, is less frequently employed and then only in the case of rich alloys. In this method, seven-eighths of the lead is removed as crystals; the method of working is otherwise quite similar.

The introduction of the Pattinson process resulted in the saving of a great deal of silver and lead. It was estimated by Pattinson (*op. cit.*) that when a 10 oz. lead is treated by the process, so that the rich alloy contains 200 ozs. of silver per ton, only 5 p.c. of the lead requires to be cupelled, and the diminution in the loss of lead in this process amounted, in Britain alone, to 300 tons. About 1830, the costs of refining were such, that the operation was only profitable when the work-lead contained 6—8 ozs. of silver per ton. Of the 45,000 tons of lead produced in England and Wales at that period,

a large proportion was poorer in silver than this minimum. The Yorkshire lead averaged 2 ozs.; the Derbyshire and Shropshire lead, 1—1.5 oz.; of the large Alston output, 16,000 tons contained 6—12 ozs. and 6000 tons only 3.5—6 ozs. of silver per ton. Altogether, some 36,000 tons a year were unsuitable for refining and, as the average silver content of this was 5—6 ozs., the pattinsonising of this amount resulted in the saving of about 200,000 ozs. of silver. Another advantage of the process is that the lead itself is greatly purified, for the frequent melting of the metal is accompanied by drossing and the removal of the scums leaves the lead in a purer condition. The amount of dross from a 20 oz. lead may be 25 p.c. of the weight of the metal. If rich in copper, the dross is liquated and the residue smelted for matte; in general, it forms an addition to smelting charges.

Attempts have been made to lessen the labour of pattinsonising by the introduction of mechanical stirring arrangements, used during the crystallisation of the metal, and tapping devices for drawing off the rich alloy from the crystals. This process of mechanical pattinsonising was replaced by the cheaper and more effective one of steam pattinsonising, designed by Luce and Rozan at Marseilles.

THE ROZAN PROCESS

In this process, steam under pressure is forced into molten argentiferous lead. The very effective stirring produced by this means, promotes uniformity in the temperature of the crystallising metal, prevents thereby the formation of crusts and furnishes a mass of small crystals of pure lead, which can be easily drained from the rich mother-liquor. Some maintain that the steam serves the further purpose of oxidising metal impurities, such as antimony, copper, and arsenic, though this effect might be referred to the air carried in with the steam. However this be, work-leads containing 0.5—0.75 p.c. of foreign metals may be submitted to the process without being first softened.

The plant is represented in Figs. 21—24.¹⁾ Fig. 24 is the plan of a battery, Fig. 21 is an elevation along the line ST, Fig. 22 a section along a line UV, and Fig. 23 a section along the line XY.

The pot marked M (Fig. 21) is simply a melting-pot, and the lower pot C is the working, or, as it is commonly called, the crystallising pot. To illustrate the working, we will

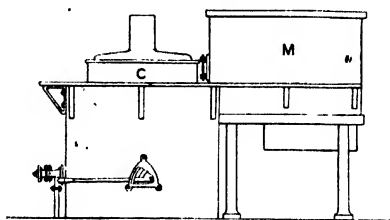


Fig. 21.—Rozan Process, Elevation.

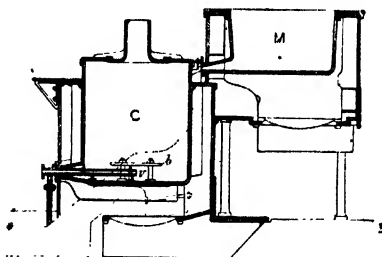


Fig. 22.—Rozan Process, Section along UV (Fig. 24).

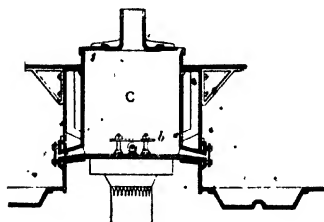


Fig. 23.—Rozan Process, Section along XY (Fig. 24).

¹ This account is taken, almost *verbatim*, from a paper by N. C. Cookson, *Trans. Newcastle Chem. Soc.*, 1877, IV., 171.

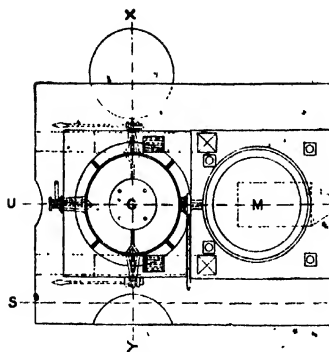


Fig. 24.—Rozan Process: Plan of a Battery.

suppose the C pot contains 14 tons of lead crystals from a previous operation, assaying, say, 80 ozs. of silver per ton, and the M pot 7 tons of original lead of similar silver content already melted; a moderate fire is set away in the firegrate of the C pot, and the contents of the M pot are skimmed; the hot lead from the pot M is then run on to the warm crystals in the C pot, and, with the assistance of the moderate fire already referred to, the whole contents of this pot (now 21 tons) are rapidly brought into a melted and working condition, when the charge is carefully skimmed; the M pot is at the same time charged with 7 tons of lead containing about 40 oz. silver per ton of lead, as this will be the assay of the crystals resulting from the operation shortly about to commence in the C pot. The fire under this pot is next drawn, and a small fire under each of the tapping spouts is set away, the object of this being to prevent the lead setting in them when tapping out the rich lead later on. Steam at 50—55 lbs. per square inch is next admitted through the valve V, and is distributed evenly through the pot by the baffle plate *b* (Fig. 22). To hasten the cooling and consequent crystallisation, thin streams of water are allowed to run on to the surface of the lead. This might be thought to cause the lead to set on the top, but the violent action of the steam entirely prevents this, and a more perfect crystallisation is effected than can be obtained

in the old Pattinson process. When the workman sees that the charge is ready, *i. e.* when about two-thirds are in crystals and one-third liquid, he taps out through spouts at either side of the C pot the rich liquid lead, the poorer crystals being retained in the pot by perforated plates. This liquid lead is run into moulds containing $3\frac{1}{2}$ tons each, and the blocks as they set are lifted out by cranes and arranged in a semicircle, where they await their turn to be again operated on. This process of crystallising, as in that of Pattinson, is repeated until the crystals are sufficiently poor in silver not to require further treatment, when, being fit for market lead, they are melted and run into pigs of the usual size, or into $3\frac{1}{2}$ -ton blocks, according to the purpose for which they are required; the rich lead is worked up until its silver contents are of the standard fit for the refinery. A large portion of the foreign metals contained in the original lead is skimmed off in the state of oxides; those from the richer charges are very dark in colour, some in fact almost black, owing to the impurities contained in them, while those from the poorer charges have the yellowish colour proper to the oxides of lead. Some, however, are carried off up the funnel above the C pot, with the escaping steam, and are deposited in the condensing chambers, of which there are several of large size. The dust contains 80—85 p.c. of lead oxide, a considerable amount of copper and antimony, and small quantities of arsenic, iron, and other metals.

The following table gives the silver assays of twelve crystallisations taken from an average of 350 operations:—

Ounces of silver per ton of lead

| |
|--|
| 570—315—202—112·5—62—33·75—19·5—10—5—2·5—1·25—14 dwts. |
|--|

The advantages of this method (summarised by Cookson) are: the expense of softening hard leads is saved; only one-fifth of the labour and two-fifths of the fuel used in the ordinary process is required; a saving in one third of the amount of dross produced. Against these merits there are two drawbacks, viz. that a large capital outlay is required, and there is a constant expense for repairs and renewals.

At Omaha, Nevada, there is a modification of the Rozan process, introduced by Tredinnick. The pots, of which there are twelve, are 7 feet in diameter and 6 feet 3 inches deep, they hold 50 tons, and each is supported by hydraulic rams, so that it can be raised and the lead or enriched alloy run into a neighbouring pot. There are two outlets to each pot, one fitted with a strainer for running off the alloy from the lead crystals, the other having a free run for pouring out the re-melted crystals. Heating is by gas, which is burnt in brick-lined jackets under the pots and the molten lead is stirred with high-pressure steam and cooled with water, exactly as in the Rozan process.

One advantage of this method is that the tapped lead does not require re-melting. Much time and labour are thus saved. The operation is done in about 40 minutes.

Newnam, in America, has recently adopted the Tredinnick method for the treatment of work-lead, containing 0.33 p.c. of bismuth, with the object of obtaining a corroding lead, with a maximum of 0.05 p.c. of bismuth, and a rich alloy, with 1 p.c. of bismuth, which can be refined electrolytically.

The alloys of lead and bismuth belong, like those of lead and silver, to the eutectiferous series, their general relations being exhibited in the equilibrium-diagram, Fig. 25.

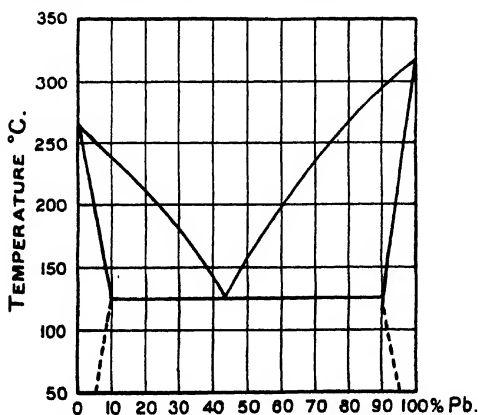


Fig. 25.—Equilibrium-Diagram of Alloys of Bismuth and Lead.
Smythe's Chemistry of Lead

They show one important difference from the lead-silver alloys, in that the solid phases, deposited on cooling, are not the pure metals, but solid solutions of these in one another, the maximum degree of solubility of each in the other being about 10 p.c. at the eutectic temperature (125°).

When a liquid alloy containing 0.33 p.c. of bismuth is cooled, crystals of solid solution separate. These, however, contain only a small quantity of bismuth at the freezing temperature of such an alloy, as is evident from the slope of the solidus curve in the diagram. Enrichment of the mother-liquor in bismuth results, but this is not so pronounced as in the case of the silver-lead alloys. Thus, the salient features of the pattinsonising of bismuth-leads are apparent, namely, the concentration of bismuth in the rich residual alloy, and the difficulty of producing a market-lead containing less than about 0.05 p.c. of bismuth.

These relations are doubtless modified, and to an unknown degree, in the case, important in practice, of ternary alloys of lead, bismuth and silver. An actual example will illustrate the much more effective concentration of silver than of bismuth, which is possible by pattinsonising such an alloy. Thus, at Freiberg, a work-lead containing 0.06 p.c. of bismuth and 146 ozs. of silver per ton, yielded a rich alloy with 0.18 p.c. of bismuth and 583 ozs. of silver per ton, and a poor alloy with 0.2 p.c. of bismuth and 0.44 ozs. of silver per ton.

THE PARKES PROCESS

The method of desilverising lead by means of zinc is now very widely used. It has practically replaced all the older methods, and is especially advantageous with leads rich in silver. It was discovered by Karsten in 1842 that zinc dissolves out the silver from argentiferous lead. Patents for this process were granted to Alexander Parkes, of Birmingham, in the years 1850, 1851, and 1852; and in 1859 the method was put in practice at Llanelly. It was subsequently tried at Tarnowitz, and, owing to the difficulties experienced

in its working, finally abandoned at both places. The chief difficulties were (1) the removal of the zinc from the desilverised lead, which could not be performed sufficiently well to make the lead marketable; (2) the separation of the silver from the zinc alloy was attended by considerable loss; (3) the recovery of the zinc from the rich lead was somewhat difficult to accomplish. These difficulties have now been in great part overcome.

In brief outline, the process consists of the following operations: Zinc is dissolved in molten argentiferous lead. A light alloy, rich in zinc and containing most of the silver, rises to the surface, solidifies before the lead, and is removed as a solid crust. From this crust, the zinc is recovered by distillation and the residual lead-silver alloy is cupelled. The desilverised lead contains a little zinc (about 0.6 p.c.) and is refined to produce market lead.

The relations to one another of the three metals concerned in the process merit further consideration. Silver mixes in all proportions with lead and zinc; lead and zinc, however, are only partly soluble in each other, the degree of solubility increasing with the temperature. Thus, if enough of each metal for mutual saturation be mixed (in the molten condition), separation into two layers takes place, the upper consisting of zinc saturated with lead, the lower, of lead saturated with zinc. For example, if 10 parts by weight of lead and 1 of zinc are mixed at a temperature of 350°, the distribution of the metals (p.c.) in the two layers is as follows:—

| | Lead | Zinc |
|-------------------|------|------|
| Upper layer . . . | 0.1 | 8.5 |
| Lower layer . . . | 90.9 | 0.5 |

Now, if silver be added to the molten lead and zinc, it is distributed between the two layers, dissolving preferentially in the zinc, so that the upper layer contains most of the silver. The following table¹) shows the composition (p.c.) of the two layers in three experiments with the triple alloy¹):—

¹ C. R. A. Wright, *Proc. Roy. Soc.* 1892, 50, 390.

| | Upper layer | | | Lower layer | | |
|-------------|-------------|------|--------|-------------|------|--------|
| | Lead | Zinc | Silver | Lead | Zinc | Silver |
| 1 | 3.1 | 58.0 | 38.9 | 96.7 | 2.0 | 1.3 |
| 2 | 3.4 | 51.6 | 45.0 | 96.4 | 1.9 | 1.7 |
| 3 | 4.2 | 40.9 | 54.9 | 93.2 | 1.3 | 5.5 |

In example 1, the lead, zinc, and silver are mixed in the proportion by weight 5:3:2; a simple calculation from these data shows that the weights of the two layers are practically identical; now the ratio of silver in the upper and lower layers is 38.9:1.3, that is, 30:1; or, in other words, about 96 p.c. of the silver has passed into the layer rich in zinc. Similar relations hold in the other two examples and generally. More recent experiments, of a similar character, indicate that the extraction of silver from lead by zinc is much more efficient than shown by these data; in other words, the partition-coefficient of silver between zinc and lead, that is, the ratio of the concentrations of silver in the two metals, is much higher, namely, of the order 300:1. The practical utilisation of this behaviour of the alloys, in the desilverisation of lead, is rendered possible by the solidification of the upper layer at a higher temperature than the lower one, so that the crusts, rich in silver, can be easily removed from the still molten, partly-desilverised lead.

It will be evident that complete desilverisation of lead by this process is impossible; but if the extraction with zinc be repeated two or three times, the amount of silver remaining in the lead is commercially negligible, being of the order of $\frac{1}{4}$ oz. per ton.

Under similar conditions of treatment, gold behaves like silver, but is even more readily taken up by zinc, so that by using a small quantity of zinc in the first treatment, the gold can be concentrated in the first crust and removed, leaving the bulk of the silver in the residual lead; for example, 200 to 300 lbs. of zinc added to a 35-ton charge removed nearly 2 oz.

of gold per ton of lead, along with the copper. Lead requires about 0.6 p.c. of its weight of zinc for saturation. Only 70 p.c. of this amount of zinc is required to extract the gold from lead which contains 0.1 oz. per ton, and the bare amount of zinc necessary for saturation of the lead suffices to remove 0.5 oz. of gold per ton. It is evident, therefore, that the principles involved in the extraction of gold and silver from lead are different, the removal of the gold depending on the formation of insoluble compounds of gold and zinc. Compounds of silver and zinc are known (e.g. Ag_2Zn_3 , Ag_2Zn_5), but we are in ignorance as to the effect, if any, they exert on the desilverising process. Three compounds of gold and zinc have been described, AuZn , freezing at 744° , Au_3Zn_5 and AuZn_8 , formed respectively at 651° and 490° from solid solution and liquor.¹⁾ The clean separation of the rich alloy from the lead is, of course, impossible in practice; much lead is carried mechanically with the crusts, even when these are squeezed in the Howard press. Poor crusts are often enriched by adding them to fresh baths of silver-bearing lead. The composition of a suitable crust for distillation is generally reckoned at 80 p.c. lead and 20 p.c. zinc and silver. An actual analysis of a crust may be quoted as typical:

| | |
|----------------------|------------------|
| Lead | 70.30 p.c. |
| Silver | 3.65 " |
| Zinc | 19.34 " |
| Zinc oxide | 2.05 " |
| Antimony | 1.11 " |
| Arsenic | 0.73 " |
| Copper | 2.25 p.c. |
| | <hr/> 99.43 p.c. |

The relatively large amount of copper, shown in this table, is an indication of the ease with which that metal is extracted from lead by means of zinc. In this respect it stands on a level with the precious metals, and its presence is undesirable, as it increases the consumption of zinc. Arsenic and antimony

¹ R. Vogel, *Zeitsch. Anorg. Chem.*, 1906, **48**, 319.

have a similar effect, so that lead has to be thoroughly purified before treatment by Parkes' process.

The process is carried out in cast-iron pots or kettles, each separately fired, holding 25—60 tons of lead. Two of these, worked alternately, are used, and two smaller liquating or draining pots, for the reception of crusts, are generally arranged alongside of them. The diameter of a 30-ton pot is about 9 feet, and the depth is 3 feet 4 inches. When it is customary to syphon the molten lead, the depth of the pot is naturally limited by the height of the barometric column of lead.

The lead is usually run direct from the softening furnace and skimmed in the pot, though some desilverisers prefer to cast the softened lead into pigs and re-melt these in the zincage pots, since, thereby, better liquation and removal of copper is effected and zinc is economised.

The metal is heated somewhat higher than the melting point of zinc (418°C.). Zinc is added either in the solid or liquid condition and well stirred for about 20 minutes by means of paddles. A mechanical device, Howard's stirrer, may be used to replace hand-labour. This is a power-driven screw-propeller, fixed in the middle of a cover, which rests on the rim of the pot. The whole arrangement is movable along an overhead track and can be placed in position for action and removed when desired. This method enables a very thorough mixing of the metals to be effected, undue oxidation being prevented meanwhile.

After stirring, the fire is damped and the alloy allowed to cool down, nearly to the melting point of lead. The crusts which are formed are lifted with a perforated paddle or skimmer, allowed to drain, and transferred to one of the smaller pots. In many works, the excess of lead is squeezed out of the crusts in a Howard press (*v. Fig. 26*). This is a cast-iron cylinder with a perforated, tilting bottom. Inside is a screw-press with toothed plunger. The mechanism is power-driven, and the whole travels on an overhead track and can be brought into position and lowered into the pot at the

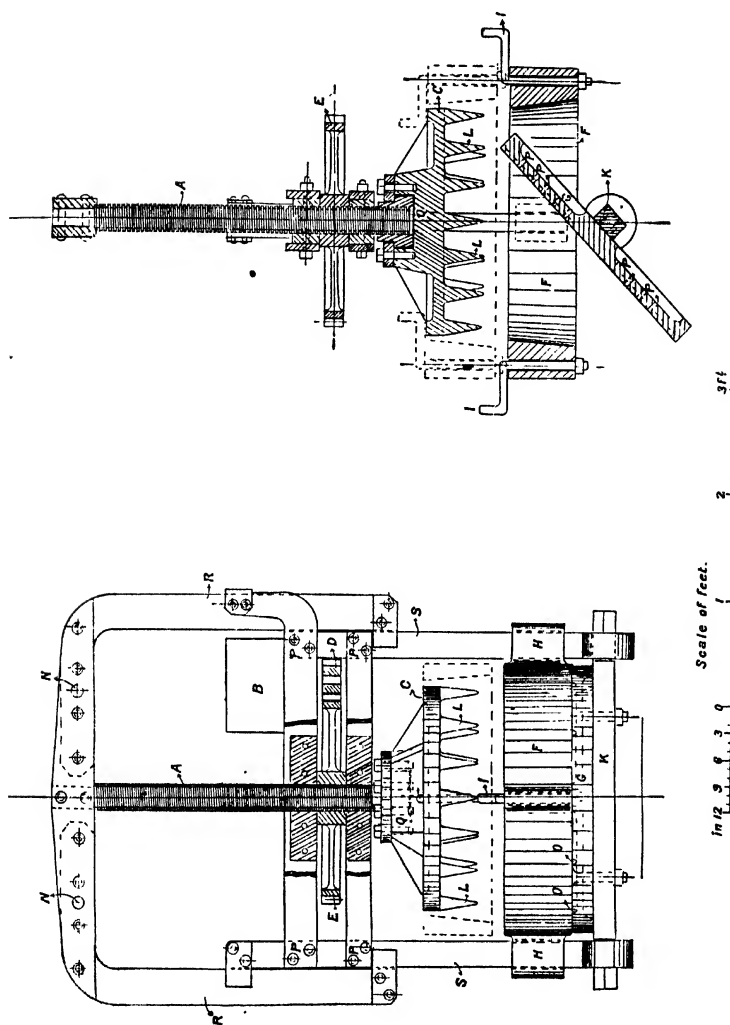


Fig. 26.—Howard Press.

(From Collins' 'Metallurgy of Lead', C. Griffin & Co. Ltd.)

suitable time, namely, when the crusts begin to form. After the press has attained the temperature of the metal, the crusts are lifted in and the cylinder raised against the plunger. The cylinder is then lowered, the plunger turned a little so that the teeth will penetrate a different part of the crust, and the pressure again applied, and this operation repeated until the excess of lead has been forced out of the zinc alloy. After the pressing is completed, the apparatus is removed and the bottom tilted, when the drained crust drops out.

After the removal of the first crusts, the pot is heated again, fresh zinc added, and the operations just described are repeated. A third, and even a fourth, zincing are sometimes necessary to complete the process.

The later crusts, which contain excess of unused zinc, serve for the first zincing of fresh lead. They need not be liquated, but are melted and cast into pigs or blocks. If necessary, zinc is added, along with these crusts, when they are used again for desilverising.

The amount of zinc required depends on the silver-content of the lead and the impurities present; of these copper has perhaps most influence on the zinc-consumption. The following table of Illings is one of many which have been compiled, though none is suitable for all varieties of practice:—

| Silver in the work-lead (p.c.) | Zinc required (p.c. of lead) |
|-----------------------------------|---------------------------------|
| 0·025 | 1·25 |
| 0·05 | 1·33 |
| 0·1 | 1·5 |
| 0·15 | 1·66 |
| 0·3—0·4 | 2·0 |

The relationship may be shown in another way, as in the table below, which is based on actual practice:

| Silver in the lead (ozs. per ton) | Ratio by weight Zinc : Silver |
|--------------------------------------|----------------------------------|
| 20 | 21·8 : 1 |
| 27 | 15·0 : 1 |
| 35 | 13·7 : 1 |
| 159 | 3·5 : 1 |
| 170 | 3·3 : 1 |
| 226 | 3·0 : 1 |
| 262 | 2·6 : 1 |

The proportions of the total zinc required, which are used for each zincing operation, vary very much in different places and with different grades of lead. Thus for a 25-ton pot of lead, assaying 550 ozs. silver, the total quantity of zinc required was 1130 lbs., and of this 430 lbs. were used for the first zincing and 450 lbs. for each of the two following zincings. In another case, 33 tons of lead, containing 300 ozs. silver per ton, were treated with zinc three times, the amounts of zinc used being 200, 700, and 700 lbs.

In the following example, the data are more complete. Three zincings were given, the first consisting of the melted third crust from the previous charge, with or without the addition of fresh zinc. The progress of the desilverising with each zincing is well shown.

| Silver assay (per ton) | | | | Amount of zinc used (lbs.) | | | |
|------------------------|-------------------------------|--------------------------------|---------------------------------|------------------------------------|----------------|---------------|-------|
| Original lead, ozs. | Lead after first zincing ozs. | Lead after second zincing ozs. | Lead after third zincing, dwts. | First zincing | Second zincing | Third zincing | Total |
| 166 | 57 | 8 | 2.5 | 3rd crust from previous charge . . | 530 | 550 | 1080 |
| 350 | 120 | 9 | 3 | 3rd crust + 200 lbs. zinc | 886 | 580 | 1666 |
| 508 | 132 | 13 | 3.5 | 3rd crust + 200 lbs. zinc | 855 | 560 | 1715 |

When a pot receives three zincings, a good deal of lead is removed with the crusts, especially if the lead is rich in silver. The level of the lead is thereby greatly reduced, and the yield of finished lead from a pot is less by, perhaps, several tons. It is advisable, in such a case, to fill up the pot with lead of good quality, low in silver, before the third zincing, so that a full charge of lead can be run, when desilverised, into the softening furnace, and thus the output of market lead can be maintained.

The zinc crusts, which have not been pressed mechanically,

are usually liquated before distillation and the liquated lead returned to the desilverising pot. The rich liquation-residues, or the pressed crusts, are then distilled in graphite crucibles, 22 inches high, 15 inches in diameter and 2 inches thick. The crucibles are heated in small furnaces fired by coke, oil, or gas, and the alloy added in batches, as it is melted down, until the right amount is charged. A hood is then luted on and a

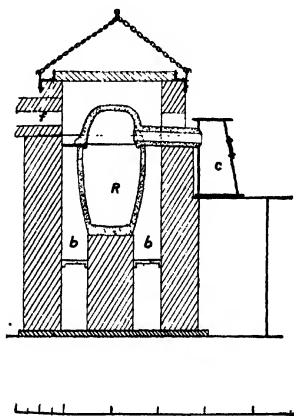


Fig. 27.—Morgan Crucible.

(From Collins' 'Metallurgy of Lead'. C. Griffin & Co. Ltd.)

condenser of sheet or cast iron attached. The general arrangement is shown in Fig. 27, where R is the crucible, *b* the fire-place and C the condenser. The zinc begins to distil at 670° , and the temperature is raised to about 1000° — 1200° to complete the distillation. The metal is run from the condenser, cast into slabs, and is used again in the process. The residual lead-silver alloy is ladled from the retort and cast into bars, which contain 2000—4000 ozs. silver per ton. The small amount of zinc which these distillery-bars contain is afterwards burnt out in the cupellation-process.

A certain amount of zinc is oxidised in the distillation-process and constitutes the 'blue powder'. This is sometimes

transferred to the zinc smelters. As the desilverised lead holds about 0·6 p.c. of zinc, the amount of zinc recovered will depend, in a large measure, on the amount used, *i.e.* on the grade of the silver lead. This is illustrated in the following table, which gives the results obtained at a large works, averaged over a long period:—

| | a. | b. | c. | d. |
|--|------|------|-------|------|
| Silver in lead (ozs. per ton) | 20 | 35 | 169·2 | 224 |
| Gold in lead (ozs. per ton) | — | — | 1·11 | 1·61 |
| Zinc used (p.c. on lead) | 1·36 | 1·49 | 1·74 | 2·09 |
| Zinc recovered (p.c. of total zinc used) | 35·3 | 38·7 | 49·2 | 58·9 |

In America, and occasionally in other countries, the tilting furnace of Faber du Four is used for distilling zinc crusts. This furnace consists of a firebrick box in a cast-iron frame. The retort is laid in a sloping position in the furnace and the neck protrudes outside and is fitted with a condenser. The furnace is mounted on trunnions and can be tilted by hand. When distillation is complete, the condenser is detached and the alloy poured out of the retort by tilting the furnace.

The desilverised lead, containing about 0·6 p.c. of zinc, is tapped, pumped, or syphoned from the pot, and run into an improving furnace placed at a lower level, where it is kept at a red heat for several hours and occasionally skimmed. The progress of refining is watched by withdrawing small samples, which are cast in a mould, and from the appearance presented on cooling, the state of the lead is determined. When thoroughly refined, the lead is tapped into a cast-iron pot and then run into pig moulds.

The method of treating work-lead for the recovery of silver and gold may be illustrated by two examples.

At Port Pirie¹), the work-lead produced by the smelting of ores from Broken Hill is run into a drossing furnace and the copper removed. The dross amounts to 5 p.c. of the bullion

¹ *The Metal Industry*, 1917, 463.

and contains 10 p.c. of copper. The bullion is then tapped into an improving furnace of 65 tons' capacity and drossed for 12 hours. The antimonial scum (6—7 p.c. antimony) thus produced is smelted in a reverberatory furnace and yields a richer slag containing 12—13 p.c. antimony; this is then smelted in a blast furnace for antimonial lead.

The purified bullion is submitted to Parkes' process. The first zincing extracts the gold, the second yields a crust containing 1500—2000 ozs. of silver per ton, and the third reduces the silver in the lead to 0.4 oz. per ton. The desilverised lead, containing 0.6 p.c. of zinc, is refined in a softening furnace for 12 hours, and yields market lead of the composition: lead, 99.9917; silver, 0.0012; copper, 0.0001; zinc, 0.001; antimony, 0.006 p.c.

The first zinc crust is melted in a reverberatory furnace, with litharge derived from the cupellation-process. Zinc is converted into oxide, which forms a slag with the litharge; this is removed and smelted in the blast furnace to recover lead and silver. The lead is tapped from the reverberatory into a desilverising pot and again treated with zinc. This yields a crust enriched in gold. The alloy is distilled in graphite crucibles to remove the zinc and the residual gold-silver-lead alloy cupelled for doré bars, which contain 2.5 p.c. of gold. The gold is parted by sulphuric acid, and the silver sulphate reduced to metal on a cupel with fine coal, the metal being 993 fine.

The second crust is distilled and yields zinc, which is used again in the process, and distillery bars containing 2500 ozs. per ton of silver. These are cupelled for silver. The third crust, being poor in silver, is used for zincing fresh base bullion.

At the Selby Smelter, California¹), the work-lead is softened in reverberatory furnaces of 70 tons capacity, the first copper dross being removed and smelted for a leady copper matte, which is roasted and returned to the blast furnace, the later antimony-rich scums being smelted in a blast furnace for

¹ T. A. Rickard, *Min. and Scient. Press.*, 1916, p. 505.

antimonial lead. The softened bullion-lead, carrying 150 ozs. of silver and 7 ozs. of gold per ton, is tapped into desilverising kettles, 3 feet deep and 10 feet in diameter, holding 60—65 tons, and is there stirred with zinc.

The crusts are squeezed in a Howard press and then contain 22 p.c. of zinc, 10 p.c. of gold and silver, 3 p.c. of copper and 65 p.c. of lead. They are distilled in graphite crucibles, yielding thereby a doré alloy containing 4000—6000 ozs. per ton. This is cupelled and the precious metals in the residual alloy parted by means of concentrated sulphuric acid. The insoluble spongy mass of gold is washed and melted down in graphite crucibles; the silver is precipitated from its sulphate solution with copper, washed thoroughly, squeezed and melted and cast into bars; the copper sulphate solution is worked for bluestone.

The desilverised lead is syphoned from the kettles into a reverberatory furnace, where the zinc is burnt out. The skimmings of litharge are smelted in a blast furnace and the lead, when softened, tapped into a moulding kettle, where it is cast into fifty moulds, arranged in a three-quarters circle in front of the kettle.

CHAPTER VII

CUPELLATION OR REFINING

The ancient process of cupellation, which is the one still used in order to the extract silver (and gold) from the rich alloy prepared from work-lead by the Pattinson or Parkes process, depends on the difference in behaviour towards the oxidising action of air of the various constituents of the alloy.

Molten lead is oxidised by air at the melting temperature of the metal (328°) and a scum of solid oxide is formed on the surface of the lead. If the temperature be high enough (ca. 900°), the litharge produced is melted, and can be blown from the surface by a blast of air, exposing thereby a fresh surface of metal and greatly increasing the rate of oxidation.

Silver, when molten (m.p. 962°), absorbs oxygen with

great rapidity, and to an extent which depends on the temperature of the metal and the partial pressure of the oxygen. The precise relationship of solubility to pressure is shown in the following table:¹⁾

| Solubility of oxygen in molten Silver at 1075° | | |
|--|--|----------------------|
| Pressure of Oxygen (mm. Hg) | Volume of Oxygen in c.c. at N. T. P. absorbed by 10.87 grams of Silver | $\sqrt{\frac{P}{m}}$ |
| P. | m. | |
| 1203 | 26.91 | 1.29 |
| 760 | 21.01 | 1.31 |
| 488 | 17.02 | 1.30 |
| 346 | 14.53 | 1.28 |
| 209 | 11.75 | 1.23 |
| 150 | 10.09 | 1.21 |
| 128 | 8.87 | 1.28 |
| 39 | 4.75 | 1.31 |

From the constancy of the figures in the third column, it is clear that the concentration of oxygen in the silver is proportional to the square root of the gaseous pressure of the oxygen, and it follows from this, by the application of the mass-law, that the dissolved oxygen is in a different condition from gaseous oxygen; if the latter be represented as molecular, symbolised by O_2 , then the former is either atomic, as indicated by the symbol O , or combined in some such form as Ag_2O or Ag_4O .²⁾ The mass-law does not enable us to decide between these alternatives, but there is other evidence which favours the view that the dissolved oxygen is bound as an oxide, which is more probably Ag_4O than Ag_2O .

At the partial pressure of oxygen in air (150 mm.), 10.87 grams of silver dissolve 10.09 c.c. of oxygen at 1075°; at the melting point of silver, this would be somewhat greater and may be placed at 11 c.c. of oxygen per 10 grams of silver;

¹ Sieverts and Hagenacker, *Zeitschr. physik. Chem.*, 1909. **68**. 115.

² F. G. Donnan and T. W. A. Shaw, *Journ. Soc. Chem. Ind.*, 1910, **29**, 987.

whence it follows that 1 c.c. of silver dissolves about 12 times its own volume of oxygen (reckoned at N.T.P.) at its melting point. This agrees fairly well with an old observation of Chevillot (1820) that 1 c.c. of silver, saturated with atmospheric oxygen, gave up 10.5 c.c. of oxygen on solidifying. Assuming that the dissolved oxygen is present as an oxide, this would imply that the saturated solution contained, per 100 grams of silver, 2.32 grams of Ag_2O or 4.48 grams of Ag_4O . The solution is thus fairly dilute¹), which may account for the relative stability of the silver oxide when in solution; but the high dissociation-pressure of the oxide brings about its immediate resolution into silver and oxygen, as soon as the compound separates in the solid state. Thus the phenomena of the spitting or sprouting of silver²) at the moment of its solidification can be understood. In practice, it leads to loss in the cupellation furnace, by the forcible ejection of solid particles of silver, and it hampers the casting of silver. It can be overcome in part by the addition of a deoxidising agent,

1 The freezing point of silver is depressed 7° by saturation with oxygen under atmospheric conditions. Donnan and Shaw (*op. cit.*) calculate the depression from the above data, and the known latent heat of silver, as 10.4° , which is in fair agreement with the experimental results when the sources of error are considered. It is not improbable that the system silver-silver oxide resembles that of copper-copper oxide. The latter is eutectiferous, the eutectic containing 3.5 p.c. of cuprous oxide and freezing about 18° below pure copper. From the late occurrence of sprouting in the crystallisation of silver, it would thus appear that, granting the above assumptions, the silver-oxygen alloy is richer in silver than the eutectic. On cooling, silver separates first and the liquor becomes enriched in oxygen (oxide) until the eutectic composition is reached. Only when this happens does silver oxide appear as a solid phase and, being unstable, is immediately decomposed. On this view, the sprouting is contemporaneous with the last stages of the freezing of the alloy, namely, the solidification of the eutectic.

2 H. C. and L. H. Hoover point out in their translation of Agricola's *De Re Metallica* that this phenomenon is referred to by Aristotle (*Problems*, XXIV, 9) in these words: "What is the reason that boiling water does not leap out of the vessel silver also does this when it is purified".

like copper or aluminium, by covering the metal with charcoal, or by directing a current of steam on to the surface of the metal.

As the sprouting of silver is confined to the pure metal and is not observed when this is alloyed with lead, it seems very probable that silver oxide and lead are constantly reacting during the cupellation-process, the silver thus acting as a carrier of oxygen from air to lead, and that the catalytic action of silver oxide is an important factor in the production of litharge from lead, for the base metal, when pure, is difficult to oxidise.

The lead-bullion submitted to cupellation often contains metallic impurities, the oxidation of which is doubtless facilitated both by litharge and silver oxide. Of these, the first to become oxidised are tin, iron and zinc; arsenic and antimony follow these, and the most difficult to remove are copper and bismuth. The persistence of the copper is to be explained by the reducing action which lead exercises on cuprous oxide, aided by the solvent action of silver on copper, which results in the retention of much more copper in solution than would be possible in the case of a simple binary alloy of lead and copper, and thus, by bringing it into intimate contact with lead, affords it protection from permanent oxidation. The old observations of D'Arcet¹) confirm this. He found that the ratio of lead to copper, requisite for the cupellation of a silver-copper alloy, increased with the proportion of silver in the alloy; thus, for an alloy of 95 silver: 5 copper, the ratio of lead to copper is as high as 60:1, whereas, for one of 10 silver: 90 copper, the ratio is only 18:1.

Bismuth behaves like lead itself and can, in fact, be used instead of lead for refining silver. In the ordinary treatment of silver-lead containing bismuth, this metal is found concentrated in the later portions of the litharge. If this be freshened or reduced and the metal again cupelled, considerable enrichment of bismuth is effected, and the material can then be

1 See Berthier, *Traité des Essais*, p. 725.

worked up, by the wet method, for the extraction of bismuth or its compounds. Molten oxide of bismuth penetrates the cupellation-hearth readily and increases the loss of silver.

Some of the properties of litharge are important in their bearing on cupellation. It is at once an oxidising agent and a powerful base and thus aids, as we have seen, in the oxidation of the impurities in the lead bullion. When the oxidation of these produces acidic oxides, as in the case of arsenic and antimony, these oxides are fixed as lead salts. Many basic oxides are slagged by litharge and their removal thus facilitated. The quantity of litharge required for this purpose varies according to the nature of the oxide; thus, 1 part by weight of cuprous oxide, zinc oxide and ferric oxide require 1.5, 8 and 10 parts, respectively, in order to flux them. Silver is stated to be soluble, as oxide, in litharge to the extent of 3—6 p.c., the melting point of the litharge being reduced thereby 45°.¹) This however, is not likely to be a factor of importance in cupellation. By reason of the strongly basic properties of litharge, care must be exercised in the selection of suitable materials for making cupellation-hearths. Bone-ash, marls (clayey limestones) and Portland cement are the materials most favoured.

The necessity for renewing the cupellation-hearth frequently has been met by two radically different devices. In England, the furnace is so arranged that the hearth can be withdrawn, re-made, and placed in position for a fresh operation; in Germany, the hearth is fixed, but the roof can be lifted and swung aside, so as to allow of ready access for the purpose of repairing the hearth. These are the distinguishing features of the English and the German methods of cupellation. Differences affecting the conduct of operations will be dealt with in the description of the two.

THE ENGLISH PROCESS

The furnace is a reverberatory, constructed with a large fire-grate compared to the size of the hearth, since a high

¹ E. J. Kohlmeier, *Chem. Zeit.*, 1912, **36**, 1079.

temperature has to be maintained for a long period of time, and risk of the charge freezing must be avoided. The hearth or test (Lat: *testa*, a brick or tile) is composed of bone-ash mixed with about one tenth to one fortieth its weight of pearl ash. This material, finely ground and moistened so that it can be balled in the hand, is filled into an elliptical iron test-ring (Fig. 28), the longer axis of which is 4 feet, the shorter 2 feet 6 inches and the depth 4 inches, with a skeleton bottom of

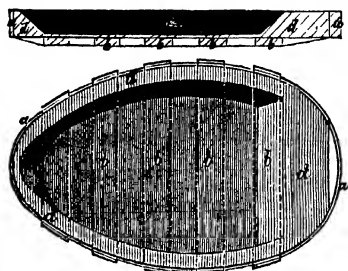


Fig. 28.—English Cupellation.

5 bars (*b*) each 4 inches wide. It is rammed in full and level with the top of the ring, and then shaped with a sharp spade or trowel into the form of a flat dish, with a breast, *d*, at one of the longer ends, across which is cut a channel, or gateway, 1 inch wide and three quarters inch deep, through which the molten litharge can escape. By boring a hole through the breast, or by cutting away a portion of the hearth-material between it and the test-ring (as shown in Fig. 28), provision is made that the escaping litharge does not come in contact with iron.

Before being used, the test is allowed to dry thoroughly in air; it is then placed on an iron wagon and run into position under the furnace, being tightly wedged against an iron ring built into the masonry. The general arrangement adopted is shown in Figs. 29 and 30, which illustrate the method of working two furnaces together. The tests are placed at *a*. *a* one of them is shown resting on the wagon *b*; *c.c.* (Fig. 29)

are melting pots for alloy which is to be cupelled, from which the molten metal runs to the hearth along the gutters *d.d.* The blast enters at *e.e.* through oval nozzles, bent slightly downwards and projecting over the edge of the test, and its direction is at right angles to the course of the hot gases which pass from the grates *g.g.* to the flues *i.i.* and thence to the chimney-stacks *k.k.*

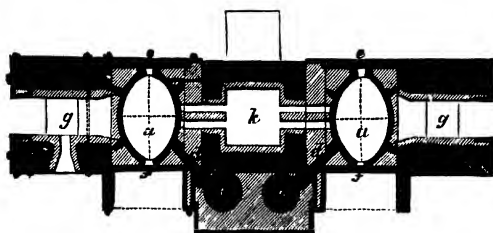


Fig. 29.—English Cupellation.

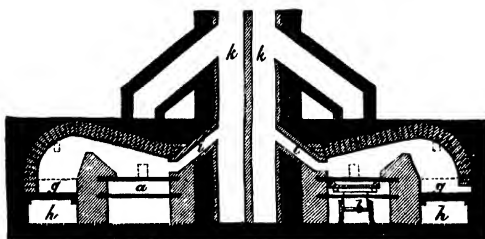


Fig. 30.—English Cupellation.

When the test is in position, the fire is lighted in the grate and the temperature gradually raised to that of bright redness. The hearth is then filled with molten lead, the blast turned on and adjusted so that the greater part of the lead surface is covered by molten litharge. This prevents undue loss by volatilisation. The molten litharge is blown through the gateway and falls into an iron pot placed to receive it outside of the furnace. Fresh lead is fed in as the level sinks in the test, new gateways are cut as required, and about 4 tons of lead are worked off in 16—18 hours with the production of a rich alloy, containing about 8 p.c. of silver.

This alloy is then tapped off, by boring a hole through the bottom of the test, and collected in an iron pot, run on wheels under the test bed; the hole is repaired and a fresh charge of argentiferous lead introduced. The enriched alloy is worked up, in a similar manner on a fresh test, until all the lead is oxidised and the silver is fine. It may be cast directly into ingots by piercing the bottom of the test, as in the former case, or it may be cooled with water and withdrawn from the furnace in the solid condition. The plate, in the latter case, is detached from the test and brushed with an iron brush to remove litharge, slag or bone ash.

By this method of treatment, a good deal of the litharge, being produced from a poor alloy, carries with it but little silver. The rich litharge from the later stages is collected apart and, as it may contain 20 ozs. of silver per ton, is treated for the recovery of that metal by reduction and desilverisation of the lead. For the purpose of reduction, a small reverberatory furnace 6 feet long by $5\frac{1}{2}$ feet wide is used; the sole slopes from the fire-bridge to an opening near the flue, where the escaping lead passes along a gutter to a receiving pot placed outside of the furnace. The hearth is covered with a bed of small coal which is ignited and the litharge, broken into lumps and mixed with a little coal is added. The reduced lead trickles away through the ashy filter beneath into the metal pot; the charge is turned over from time to time and, when the reduction is complete, the litharge slag is raked out and smelted in a slag-hearth. About 3 cwts. of coal are required to produce 1 ton of lead. Old test bottoms which become partly soaked with litharge are broken up and screened, the unaltered bone-ash used in the preparation of fresh tests and the leaded portions smelted for an impure "test-bottom lead" in the slag-hearth.

The loss of lead on refining and reduction in this way is 8 p.c. when the test-bottoms and litharge slag are not worked up, or about 6 p.c. when the lead is recovered from these products. The loss is least when the operation of cupellation is performed at a low temperature, but, on the other hand, if

the charge be not hot enough, more silver is carried away by the litharge. The loss of silver is less than 1 p.c.

The older English method just described has been developed in several directions in recent times, though none of the changes is of fundamental importance. The tests are sometimes rectangular in shape, with rounded corners, so that a greater surface of metal is exposed to oxidation; the size has also been increased, some of the larger ones being 7 by 5 feet. Efforts to minimise corrosion by the litharge have resulted in cooling devices being applied to the tests, in the form of water-pipes or water-jackets. The old method of supporting the test on two iron-bars, and adjusting it by means of iron wedges, has been supplanted in some places by suspending it from the roof by means of a differential pulley, and one advantage of this system is that the level can be altered with the progress of cupellation, so that the litharge flows away without the necessity of deepening the gateway.

The use of marl, or an artificial mixture of limestone and clay, similar in composition, has in great measure replaced the more expensive bone-ash; Portland cement is frequently used and, occasionally, the highly refractory, though costly, magnesite brick.

The first concentration of the lead-bullion is usually up to 60—70 p.c. of silver, the level of the alloy in the test being maintained constant by the melting down of bars which protrude through the back of the furnace. The fining of this enriched alloy is accomplished in a smaller finishing-furnace, where the methods employed are quite similar to those used in the concentration-process. The crude silver, left after the oxidation of the lead, is refined either by exposing it long enough to a blast at a high temperature, a little bone-ash being sprinkled on the surface to absorb impurities, or by the addition of sodium nitrate, or by adding a fresh charge of lead and repeating the cupellation. By any of these methods, the impurities in the silver which are retained most tenaciously, namely, copper and bismuth (in some cases, tellurium also) are oxidised and the pure silver, up to 997 fine,

is obtained. This is covered with charcoal to prevent or minimise spitting and either ladled or poured into moulds. Test bottoms, litharge and flue dust are now usually added to ore-charges for smelting in the blast-furnace.

THE GERMAN METHOD

The typical furnace used in the German method of cupellation is a round-hearthed reverberatory and is illustrated in Figs. 31. The movable roof is shown at *b*; it is a flat dome-shaped iron framework, fitted with fireclay tiles held together by iron rivets, and is suspended by chains from a crane, so that

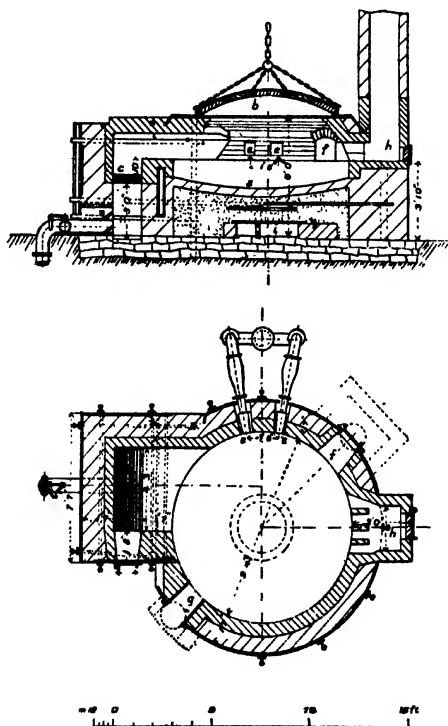


Fig. 31.—German Cupellation.

(From Collins' 'Metallurgy of Lead', C. Griffin & Co. Ltd.)

it can be lowered into position over the hearth, or raised and moved aside; *c* is the grate, beneath which is a blast pipe for the admission of low pressure blast; it is separated from the hearth by an air-cooled fire-bridge. The hearth has five openings; the litharge-notch at *g*, the flue *h*, the working door *f*, and two for the blast-pipes. These are inclined so that the air-currents meet about the middle of the hearth, and the litharge-notch is placed somewhat to one side of their medial line, with the object of lessening the amount of silver carried away by the litharge.

The lower part of the hearth is made of fire-brick and has a vault beneath for cooling purposes; over the fire-brick is a layer of slag, and upon this the working-bottom is constructed of marl, 8 inches thick, damped and well beaten down with iron rammers. The shape is saucer-like and a groove is cut across the bottom for the collection of the silver. After carefully drying, the charge of 10 tons of silver-lead is placed on the hearth and slowly melted down. A coppery dross (*Abzug*) appears on the surface and is drawn off with a piece of wood. The blast is then turned on (200—300 cubic feet per minute at a pressure of 8 ozs. per square inch) and a scum of very impure litharge, usually rich in arsenic and antimony (*Abstrich*) is formed. This runs off through the notch and is succeeded in turn by litharge, pure enough to be marketable. Towards the end, this litharge carries appreciable quantities of silver (0.02 p.c.) and is gathered apart, so that the precious metal may be extracted. As the level of the metal in the bath falls, the notch is deepened to enable the litharge to flow continuously, and, at the same time, to leave enough in the furnace to cover the greater part of the surface of metal. By this device, the volatilisation of lead is checked.

When the litharge-film becomes thin, it exhibits the beautiful play of colours known as 'flowering', which is presently followed by the flashing-out (brightening) of the mirror-like surface of the silver (*Blicksilber*). The silver is crude and is refined either in a smaller cupellation furnace, or by means of silver sulphate, as described later.

The typical German process thus differs from the English in that the hearth or test is made much bigger to accommodate the whole charge at once, and, as a consequence, the earlier stages of the operation result in the purification or softening of the lead, and a portion, about one third, of the litharge is pure enough, and has a silver-content low enough, to be marketable. The steady feed of the alloy during the English process, of necessity results in the diffusion of the impurities through all the fractions of litharge, so that none of these is pure enough for marketing.

There are various modifications of this typical process. The shape of the hearths may be oval or rectangular and their capacity greatly increased, and the English plan of adding part of the silver-lead during the operation is sometimes adopted. A common practice too, is the addition (*Eintränken*) of silver ores, metallurgical products rich in silver, silver sulphide from the wet extraction of silver ores, and such like materials, to the lead bath, whereby the constituents other than silver are slagged with the litharge, and the silver passes into the lead and is left on the hearth at the end of the cupellation.

As an example of German cupellation, the results at Müsen and Przibram may be quoted.¹⁾ At Müsen, on a hearth 10 feet in diameter, 25 tons of silver-lead are worked off in 300 hours; charging occupies 3 hours, melting 27, removal of dross 9, of scums 144, of litharge 117. From 100 parts by weight of the charge there are obtained 7.6 of dross, 21 of scums, 52 of impure litharge, 30 of pure litharge and 0.28 part of crude silver.

At Przibram, in Bohemia, 25 tons of work-lead, with 0.52 p.c. silver, are cupelled in 80 hours. The times occupied in the various stages are: making the hearth and charging 8 hours, melting the charge 16, removal of dross 6, of scums 9, of litharge 41 hours, during 23 of which marketable litharge, containing only 0.004 p.c. of silver and amounting to 36 p.c. of the whole, is obtained. The coal-consumption is 20 p.c. of

¹ Schnabel, p. 729, 732.

the weight of work-lead and the furnace is worked by 2 men on eight-hours shifts. The loss of silver is 0.8 p.c., the loss arising during the working up of the products not being included.

The composition of the various products of cupellation varies within such wide limits that the published analyses, without further information, convey but little meaning. The common impurities, copper, arsenic, antimony, iron and zinc are present in drosses and scums, along with varying quantities of litharge. The crude silver usually contains from 90—95 p.c. of silver, the chief impurities being lead, copper and bismuth.

The refining of the crude silver is now usually accomplished by utilising the discovery of Roessler, that silver sulphate (m.p. 651°), added to the molten alloy of silver, lead and bismuth, oxidises the lead and bismuth, and is itself reduced to metallic silver, sulphur dioxide being evolved. The operation is carried out in a graphite crucible, holding about 700 lbs. of crude silver, and heated in a wind-furnace. The silver sulphate, in amount about twice as much as the base metal present, is added in three or four batches to the molten alloy, stirred in, and the slag, stiffened by covering the surface with powdered quartz, removed. Vigorous bubbling takes place during the process, presumably due to the escape of sulphur dioxide. The earlier slags are rich in lead, the later ones in bismuth, and the recovery of the bismuth from these is simpler than by the treatment of test-bottoms and cupellation-litharge. This constitutes one of the merits of the process.

The analysis of a slag by Hampe shows 2 p.c. of silver and 58 p.c. of silica, phosphoric acid and oxides of iron, aluminium calcium, magnesium, potassium and sodium—all materials added in the process or derived from the crucible and tools. Deducting these and calculating the remainder to 100 p.c. the results are: $\text{PbO} = 78.3$, $\text{Bi}_2\text{O}_3 = 14.0$, $\text{Ag}_2\text{O} = 4.8$, $\text{Cu} = 1.0$, $\text{SO}_3 = 1.5$, $\text{S} = 0.4$, and a trace of antimony. Thus over 90 p.c. of the products of the reaction between the metals and silver sulphate consists of oxides of lead and bismuth. The high content of silver is noteworthy, assuming

that this is present as oxide and not as metal mechanically included. The amount of sulphur trioxide present is only equivalent to about 5 p.c. of lead sulphate.

ELECTROLYTIC REFINING

This process, the latest competitor with the long-established methods for the desilverisation of lead, resembles that of Pattinson in so far that its object is to remove pure lead from the argentiferous alloy, and to effect thereby concentration of silver in a small residual fraction. The method by which this is achieved is, however, radically different, and the conditions of its applicability enable the crude work-lead to be treated directly, without the preliminary purification which is all essential in the Pattinson process.

When a salt of lead, say PbX , where X is a bivalent acidic radicle, is dissolved in water, it is *ipso facto*, according to the ionisation-hypothesis, resolved into the two electrically charged ions, Pb^{++} and X^{--} . This reaction is reversible, and an equilibrium is established between the electrically-neutral salt and its two ions, which depends on the nature of the substances, the degree of concentration, the temperature and the presence of other ions. If now two electrodes be dipped into the solution and a difference of potential established, these ions move towards the electrodes of opposite polarity, their charges are neutralised on contact and the radicles set free. According to their nature, and that of the electrodes and solution, they may remain as such, or they may enter into secondary reactions.

Suppose that the solution of the salt PbX is to be electrolysed and that the electrodes are made of lead. Lead ions, discharged at the cathode, yield a deposit of metallic lead; X -ions discharged at the anode may react with water or with lead; in the latter case, the salt PbX is regenerated, and the quantity of lead dissolved at the anode exactly equals that deposited at the cathode. The effect of the passage of the electric current, in such conditions, is thus to transport lead from anode to cathode, through the agency of the ions.

If the anode be made of impure lead, the results are the

same, so far as the transportation of lead is concerned. The behaviour of the other metals, present as impurities, will depend on their ability to form soluble salts with the radicle X and, in the event of that taking place, the possibility of the salts entering into the electrolytic process, and thereby contaminating the cathode deposit, will be determined by the potential difference between the electrodes.

For the practical success of a process of this kind, therefore, certain conditions must be fulfilled. An electrolyte must be chosen which does not give rise to objectionable secondary reactions when electrolysed. Most of the salts of lead are of this character, since the anion when discharged, brings about oxidation, and lead peroxide is deposited at the anode. A salt fulfilling the conditions must also be readily soluble in water, and its solution must have a high conductivity, otherwise the capacity of the plant will be limited and much electrical energy will be consumed and lost in the process by conversion into heat. These, and other practical difficulties stand in the way of refining lead by electrolytic methods.

One of the earliest attempts to develop an electrolytic process was by Keith in 1878. The electrolyte was a solution containing 20 grams of lead sulphate and 180 grams of sodium or ammonium acetate per litre; the anodes of work-lead were hung in muslin bags to collect the slime which became detached during the electrolysis. Much difficulty was experienced owing to the incoherency of the cathode deposit. There is a tendency for the lead to grow in long crystals, which enclose mother-liquor difficult of removal at a later stage, and also cause short-circuiting. Efforts to overcome this difficulty by the rapid rotation of the cathode, or by addition of colloids to the bath were only partly successful. The use of acetates of lead and potassium by Tomassi did not meet with success, for the reason, apparently, that secondary reactions occurred, which gave rise to polarisation.

The discovery by A. G. Betts¹) of the suitability of

¹ U. S. Pat. 1902. 713277. See also *Lead Refining by Electrolysis*, A. G. Betts, 1908.

the fluosilicate of lead for electrolysis made possible the practical development of the subject. The crystallised salt, $\text{PbSiF}_6 \cdot 6\text{H}_2\text{O}$ melts at 60° in its water of crystallisation, and dissolves at 15° in 28 p.c. of its own weight of water, yielding a stable solution of high electrical conductivity. The conductivity of solutions suitable for electrolysis in practice (5 to 10 p.c.) is considerably increased by the addition of about the same amount of free hydrofluosilicic acid, and this addition is invariably made, though it carries with it the disadvantage that silicic acid is formed from it by hydrolysis, and there is a tendency for this to be precipitated during the process. The materials are made by distilling a mixture of fluorspar and concentrated sulphuric acid, percolating the resulting solution of hydrofluoric acid, of 35 p.c. strength, through broken quartz, and allowing the hydrofluosilicic acid thus produced to act upon white lead, litharge or metallic lead.

The solution used as electrolyte contains on an average 6 p.c. of Pb and 7 p.c. SiF_6 ; lead does not accumulate in the course of working, but there is a slight loss of acid, owing to instability or side reactions, which is made good each week by the addition of fresh acid.¹⁾ Tin and zinc, and to some extent, iron, nickel and cobalt pass into solution, but only the tin, which has a similar discharge-potential to lead (the values for normal ionic concentrations being for tin, 0.008 and for lead 0.129), is precipitated on the cathode, so that a work-lead carrying tin would need to be softened before submitting it to the process. To ensure a compact deposit on the cathode, a small quantity of colloid is added to the bath. Resorcinol and hydroquinone are mentioned as suitable additions in the original patent, but in practice gelatine or glue is used, half a pound of which is needed for one ton of refined lead. The character of the metallic deposit is then satisfactory, and its specific gravity is 11.36.

At Trail, B.C. where the method is employed²⁾ there

1 T. A. Rickard, *Min. and Scient. Press.*, 1916, 941.

2 Ingalls, *Lead Smelting and Refining*, p. 270 et seqq.; A. G. Betts, *Trans. Amer. Inst. Min. Eng.*, 1904, 34, 175; T. A. Rickard, *op. cit.*

are 408 electrolytic cells, made of cement and lined with asphalt, with a capacity of 100 tons of lead a day. The electrolyte has the composition given above, and is circulated by means of rubber pipes through the vats, which are arranged in cascade-fashion, each with a drop of 3 inches to the next. The liquor is pumped up to the one standing highest and circulates at the rate of 4—6 gallons a minute. The anode slabs of work-lead are cast at the blast-furnace; they weigh 320 lbs., are 1.5 inches thick and 0.5 inch smaller all round than the cathode-plates and are reduced 80 p.c. in weight before melting again. It is advisable to retain a uniform core of metal at the end of the process, so that the slimes can be removed easily from it, and it is also an advantage for the total impurities in the anode lead not to exceed 2 p.c., otherwise the electrolytic process does not run so smoothly.

The starting or cathode sheets are 37 by 27 inches and $\frac{1}{32}$ inch thick; they are made by pouring pure lead over an inclined steel plate and are afterwards trimmed by hand. A band of paint is put along the water-line to prevent corrosion. Each vat contains 20 anodes and 21 cathodes, the former hung by lugs on the busbars, the latter wrapped round the negative leads. The distance apart is $1\frac{3}{4}$ to $2\frac{1}{2}$ inches, the current density 12—16 amperes per square foot, and the fall in potential from anode to cathode about 0.4 volt. The temperature of the baths is maintained at 30—35° by cooling with water pipes.

During each run, the cathodes are taken out and stripped twice. The anodes, when lifted, are put into a vat of water and brushed, the cores being returned to the melting-pot. The mud or slime is washed and the washings concentrated and returned to the vats; the mud is filtered at the press, dried in the flues of a furnace, and then melted in the oxidising atmosphere of a reverberatory furnace on a basic hearth of magnesite brick. At Trail, bismuth is absent from the slimes. The roasting process yields an antimonial slag, rich in silver, which is worked up for silver and antimonial lead; after removal of this slag, a dross of cuprous oxide appears, and

finally the doré bullion is left, which is parted by the sulphuric acid method. In the following table are analyses showing the composition of two samples of work-lead, and of the refined silver and anode slimes obtained from them, by the electrolytic process. The small amount of lead and the great concentration of precious metals in the slimes are noteworthy:

| | Electrolytic Refining - Examples | | | | | |
|-------------|----------------------------------|--------------|--------|-----------|--------------|--------|
| | 1. | | | 2. | | |
| | Work Lead | Refined Lead | Slimes | Work Lead | Refined Lead | Slimes |
| Lead . . . | 87.14 | — | 10.13 | 98.10 | — | 11.09 |
| Copper . . | 1.40 | 0.0010 | 9.30 | 0.18 | 0.0066 | 4.00 |
| Bismuth . | 0.14 | 0.0022 | 0.52 | — | — | — |
| Antimony . | 4.00 | 0.0017 | 25.32 | 0.61 | 0.0043 | 30.15 |
| Arsenic . . | 7.40 | trace | 44.58 | 0.17 | 0.0001 | 3.56 |
| Tin . . . | — | — | — | 0.03 | 0.0059 | — |
| Iron . . . | — | — | — | 0.01 | 0.0012 | — |
| Silver . . | 0.64 | — | 4.7 | 0.89 | 0.0009 | 31.92 |
| Gold . . . | — | — | — | 0.01 | — | 0.45 |

The process of Betts has not yet been widely used. It is much simpler in operation than the Pattinson process, which it resembles in yielding, at one and the same time, a marketable lead poor in bismuth, and a residue in which the precious metals are concentrated, but this concentrate is comparatively free from lead. Compared with the all-powerful Parkes' process, it suffers in that the cost is much greater, and the refined lead contains more silver (0.2—0.3 ozs.).

The suggestion has been made, and apparently tried with some success, to utilise lead perchlorate for the electrolytic refining of lead.¹⁾ This salt is very soluble in water, the saturated solution containing 60.2 p.c. of the anhydrous compound and having a density 1.947,²⁾ and is easily made

¹ F. C. Mathers, U. S. Pat., 1909, 931944; *Met. and Chem. Eng.*, 1910, **8**, 347; *Chem. Zeit.*, 1910, **34**, 1316. 1350.

² Mylius & Funk, *Ber.*, 1898, **30**, 1718.

from litharge and perchloric acid; during electrolysis there is freedom from polarisation since no lead peroxide is formed. The acidity falls off somewhat, owing to the conversion of free acid into the lead salt; this can be corrected by withdrawing part of the liquor, mixing it with sulphuric acid, allowing the lead sulphate to subside and returning the supernatant solution to the bath. Addition of 0.05 p.c. of peptone to the electrolyte (which contains 5 p.c. of lead perchlorate and 2.5 p.c. of free perchloric acid) gives a dense cathode deposit, $D = 11.36$, containing 99.98 p.c. of lead. The current density is 18—27 amperes per square foot.

According to Mathers¹) a smooth, coherent deposit of lead can be obtained by electrolysing a solution containing, in the litre, 100 grams of lead acetate, 25 grams of glacial acetic acid and 40 grams of ammonium perchlorate.

CHAPTER VIII

CONDENSATION OF LEAD FUME

In all the metallurgical operations which have been considered above, considerable quantities of finely-divided materials containing lead are produced and pass away with the waste gases. Formerly, little or no effort was made to retain these, with the result that much valuable matter was lost and great damage done to the surrounding country, owing to the poisonous nature of the smoke. There are two sources of origin of this smelter's smoke. Fine particles of ores, fluxes etc. present in the charge, or produced by decrepitation, are swept away with the air-current; this material constitutes the dust. Many substances, in the course of treatment, are volatilised, e.g. lead and its sulphide and oxide, zinc, arsenic and their oxides, and the vapours, on cooling, in some cases after oxidation has taken place, yield an impalpable powder which, despite the high density of some of its components, is only deposited with great difficulty. This is generally described

¹ *Trans. Amer. Electro-chem. Soc.*, 1914, 26, 99.

as fume. Though different in origin and in grain from dust, no hard and fast line between the two can be drawn in practice.

The suggestion of Watson (1778) to attempt to condense this volatile dust and fume "by making it pass through a horizontal chimney of suitable length" was adopted at Middleton Dale in Derbyshire and proved successful, the "sublimed lead" being sold to painters at £ 10 to £ 12 a ton, and this method has been utilised continually since his day and without much alteration, in the main, except as regards the length of the flues, which, in extreme cases, is as much as five miles.

To economise space, these flues are often disposed in zig-zag form. They are built of brick or reinforced concrete, arched, and of cross section from 6 by 7 feet, to 8 by 9 feet. For cleaning purposes, there are manholes at intervals, and often there is an arrangement whereby the flues can be traversed by a stream of water and the sludge collected in a settling-tank. For short flues, cooling by water is necessary. Increase of the surface-area of the walls in contact with the fume-laden gases facilitates deposition, and this may be effected by means of baffle walls, or by hanging sheet-iron plates longitudinally in the flues, as in Freudenberg's process, or parallel rows of wires, according to the suggestion of Rösing. All such obstacles necessarily slow up the gas-current, which is an advantage from the point of view of deposition of the fume, but it may result in the necessity of supplementing ordinary chimney draught by exhaust draught.

The composition of the material collected in the flues varies within very wide limits and depends upon a great many factors, among which are; the composition of the charge, the method of treatment, the temperature and composition of the effluent gases, the distance from the furnace at which the sample is taken. At Freiberg, the dust contains 40 p.c. of lead near the flues, this decreases to 30 p.c. and then rises to 36 p.c. beyond the point where lead oxide is condensed. Arsenic increases regularly with the distance from 7 to 25 p.c. Charges rich in arsenic and zinc naturally yield a flue-dust

rich in these elements; thus 36.8 p.c. oxide of arsenic is recorded from Laurium and 49.5 p.c. zinc oxide in the dust from Freiberg blast furnaces. Lead sulphide constitutes no less than 71 p.c. of the flue-dust from Carthagera. Silica (or material insoluble in acids) is highest in the dust proper, and reaches 26 p.c. in that from Denver, Colorado. In a general way, it may be taken as an index of the nature of the deposit, dust containing more than 5 p.c. and fume less than that amount. Blast-furnace flue dust comes off at a low temperature, in a reducing atmosphere, and generally contains more silica and sulphide-sulphur than the dust from reverberatories or hearths. The dust and fume from these, and from roasting and cupellation furnaces, are rich in oxidised compounds. The following analyses may serve as examples of the composition of flue dust from some of the chief operations:

| | Analyses of Flue Dust | | | | | | | |
|--|-----------------------|--------|-----------------|-----------|----------------|--------|-------------|--|
| | Ore Hearths | | Reverberatories | | Blast Furnaces | | Cupellation | |
| | Alston | Joplin | Bagillt | Tarnowitz | Freiberg | Pueblo | Praibram | |
| PbS . . . | 1.4 | 4.6 | 1.0 | — | — | S=2.5 | — | |
| PbO . . . | 58.4 | 77.3 | 62.6 | 66.4 | 27.9 | 37.6 | 64.4 | |
| SO ₃ . . . | 17.4 | 12.6 | 25.8 | 27.5 | 13.0 | 1.6 | 16.6 | |
| ZnO . . . | 13.8 | 0.7 | 1.6 | 3.8 | 49.5 | 5.3 | 0.5 | |
| As ₂ O ₃ . . . | — | — | — | — | 2.1 | — | — | |
| Sb ₂ O ₃ . . . | — | — | — | — | — | — | 11.4 | |
| (Fe, Al) ₂ O ₃ . | 3.8 | 1.0 | 3.0 | 0.5 | — | 26.3 | — | |
| CaO . . . | — | — | 3.8 | — | 7.0 | 5.3 | — | |
| SiO ₂ . . . | 5.6 | 0.2 | 1.9 | 2.1 | — | 8.6 | 4.3 | |
| Carbon . . | — | 3.4 | — | — | — | 11.2 | — | |
| | 100.4 | 99.8 | 99.7 | 100.3 | 99.5 | 98.4 | 97.2 | |

The amount of flue-dust recovered is 4 p.c. of the ore at Pertusola, 4.7 p.c. at Tarnowitz, and 4.8 p.c. at Freiberg.

Another suggestion of Watson for recovering sublimed lead "by making it meet with water, or with the vapour of water, during the ascent", has been adopted and tested in many ways. The fume-laden gas may be simply bubbled

through water, or made to pass through filters made of faggots or cobble-stones which are sprayed with water, or steam may be injected and condensed, with the object of producing a fine rain in the gas and thus washing down the solid particles. These methods have the advantage of cooling the gas quickly and thus aiding deposition of the solids, but their success is only partial, since there is difficulty in wetting a fine dry powder, the sludge produced is awkward to handle and, in the case where wet filtration is employed, the clogging of the filters interferes with the passage of the gas. Two or three of these methods will be described briefly, more from their historic interest than as representatives of successful working methods under present conditions.

Stagg's condenser consists of a large rectangular chamber divided by partitions, springing alternately from the top and bottom of the chamber, leaving free spaces above and below; the lower part of the chamber is filled with water, so that the gases pass first down one side of a partition through the water, and rising in the next compartment pass over the next partition and down again through the water. The gases are drawn through the chamber by means of air-pumps attached to the exit flue. The fume in its passage through the condenser is thus drawn through water and robbed of part of the suspended solids. This method was at one time used at Nent Head in Cumberland.

Stokoe's method formerly used at Keld Head in Yorkshire, resembles Stagg's in the division of the chamber into compartments, access from one to the other being only possible by the gas bubbling through the water on the floor. In addition, each compartment was three-storied, the floors of the two upper chambers being made of open joists, upon which faggots were laid, and these were washed by sprays of water. The gases were thus forced to traverse the filter-beds and to bubble through water and blocking of the filter-beds was prevented by the water-sprays.

The method patented by Wilson and French in 1878 and adopted at Sheffield and Hebburn-on-Tyne is illustrated in

Fig. 32. The condenser is a wooden box, *a a*, with a shelving bottom on which the fume collects, and at the lowest point a tap, *b*, by which the contents of the condenser are run off from time to time. The box is filled with water to the level of *c*. The gases are forced into the box by a fan, along the

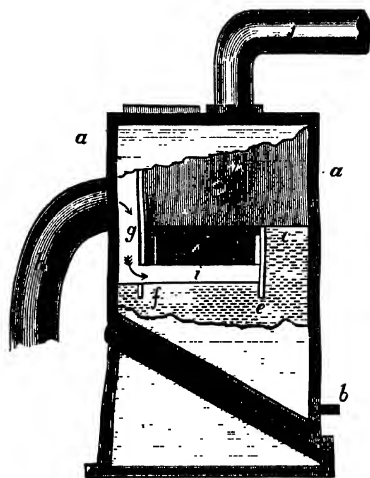


Fig. 32.—Fume Washer.

pipe *h*, which opens into a chamber *g*, formed by a partition running parallel with the side of the box. This chamber opens below, into a series of triangular tubes *i*, running across the box; these tubes are perforated above, and through the fine openings the gases are forced into the water. Near the surface of the water at *d* are fixed three or four screens made of wickerwork or copper wire, held in position by the supports *e* and *f*. The gases pass out finally by the pipe *j* in the top of the box, and are conducted by flues to the chimney. By this arrangement intimate contact between the water and the particles of the fume is insured. The fume, collecting in the lower part of the box, is drawn off into settling tanks. With three wire-gauze screens and a depth of $8\frac{1}{2}$ inches of water, French states, that at the Sheffield Smelting Company's works,

the quantity of lead and silver arrested amounts to from 95 to 98 p.c. of that contained in the smoke as it leaves the furnace.

BAG FILTRATION

Modern methods of precipitating fume are based on the treatment of the dry material and consist either in filtration through wool or cotton, or in deposition by electrostatic action.

The suggestion of Percy¹), in 1870, to filter the fume through cloth, was worked out on a practical scale by Lewis and Bartlett, and has been extensively developed. The filters are in the form of bags, 30 feet long and 16 inches wide, made with one lateral seam. The material is either cotton or wool, the latter being found more serviceable, especially when the natural oil and sweat have not been removed by washing. Hundreds or thousands of these bags are hung in a brick chamber or bag-house; the tops are tied tight, the bottoms fit round thimbles, the width of the bags and 10 inches high, in the floor of the house. Under the floor is a smaller chamber into which the furnace gases are forced by fans. The gases escape upwards, are filtered through the bags and pass into the open air through ventilators in the roof of the bag-house. The fume is detached from the fabric periodically, usually once in 24 hours, either by shaking the bags, or by causing them to collapse by suction. It falls to the lower chamber and when a layer 2 feet thick has collected, the furnace gases are diverted and the powder is ignited by a small fire. The fume, containing much oxidisable matter, burns easily and yields a grey cinder suitable for smelting in the blast furnace.

At the Murray Plant, Utah, where the system was first installed, in 1906, the bag-houses are 216 by 90 feet and 60 feet high. There are 4000 bags with a surface area of 570,000 square feet, which cope with 165,000 cubic feet of gas per minute, *i.e.* 1 cubic foot of gas passes through 3.5 square feet of filter per minute. Fig. 33 is a diagram, which is self-ex-

¹ *Metallurgy of Lead*, p. 449.

planatory, of a bag-house at the Globe Smelting Works, Utah. It is stated that 1000 square feet of filtering surface are necessary, in general, for one ton of ore, and the best temperature for filtration is variously given as 80° — 120° C. Gases from roasters are not suitable for bag-house treatment, as the

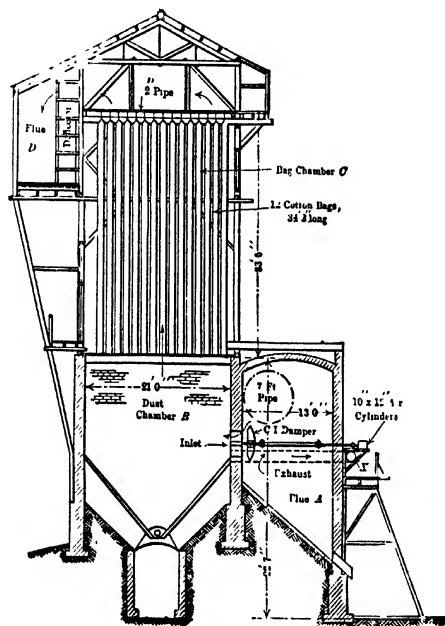


Fig. 33.—Bag House.

(From Hofman's 'Metallurgy of Lead'.)

oxides of sulphur rot the fabric. The life of cotton bags at Utah is 17 months and of woollen bags 4 years. At these works, 1.27 p.c. of the lead and 0.063 p.c. of the silver in the charge are recovered from the bag-house, and the fume contains: lead, 52.5; arsenic, 14.2; sulphur, 5.4; zinc, 3.0; antimony, 1.6 p.c.

At St. Louis, hearth-smelting yields twice as much bag-house fume as flue-dust. The burnt fume contains 70 p.c. lead

and 5.9 p.c. of sulphur; the dust, 62 p.c. lead and 11.1 p.c. of sulphur. The lead in these products is combined as follows¹⁾:

| | Flue dust (p.c.) | Burnt fume (p.c.) |
|-----------------------|---------------------|----------------------|
| Lead sulphate | 18.9 | 53.6 |
| Lead sulphide | 55.4 | 1.2 |
| Lead oxide | 2.0 | 41.5 |

The filtration-plant at Midvale, Utah, has a filtering-surface of 324,000 square feet and deals with 60,000 cubic feet per minute, which is in the ratio of 5.4 square feet of filtering fabric to 1 cubic foot of gas per minute. Fume from the roasting furnaces averages: Pb = 40, As = 12 p.c. Ag = 10 ozs. per ton, and fume from the blast furnaces: Pb = 20, As = 40 p.c. Ag = 1 oz. per ton. The method adopted here with the gases from the roasting furnaces which, in their raw state, contain so much sulphur trioxide that they speedily rot the bags, is to blow in finely-divided slaked lime and zinc oxide. The admission of these bases into the fume, cooled to 120°, before its entrance into the filtering-chamber, ensures the neutralisation of the corrosive sulphur trioxide. Lime is cheaper than oxide of zinc but not quite so effective; the major part of the neutralisation is thus done by means of lime and the completion of the process by means of zinc oxide.²⁾

ELECTRICAL PRECIPITATION OF FUME

The clearing of a smoky atmosphere by the discharge of electricity from pointed electrodes was observed by Hohlfield in 1824 and again by Guitard in 1850. Strangely enough, these early observations seem to have been completely overlooked and the phenomena to have escaped re-discovery until the early eighties of last century, when attention was again drawn to them independently by Aitken and Lodge.³⁾

1 Newnam, *Trans. Amer. Inst. Min. Eng.*, 1916, 2139.

2 Sprague, *Eng. Min. Journ.*, 1910, 89, 519.

3 J Aitken, *Proc. Roy. Soc. Edin.*, 1884, 12, 440; Sir. O. Lodge and J. W. Clark, *Nature*, 1883, 28, 297; Lodge, *Phil. Mag.*, 1884, 17, V., 214; *Brit. Ass. Rep.*, 1895, 743; *Journ. Soc. Chem. Ind.*, 1886, 5, 572; For historical notes see Lodge, *Nature*, 1905, 71, 582.

Both of these investigators saw clearly the possible application of their experimental work to the practical treatment of industrial and domestic smoke of various kinds. Aitken, for example, tried the effect of discharging electricity into the smoke of a chimney. "This also" said he "produced a marked diminution of the blackness of the escaping smoke. The supply of electricity of a sufficiently high potential is however a difficulty for the present." The industrial application of the method, patented by Walker¹), was tested in 1885 by Hutchings and Lodge²) at the Bagillt lead works of Messrs. Walker, Parker & Co. and the experiments, in which two power-driven Wimshurst machines and a system of metallic points were used, were apparently successful in a small way, but failed on a large scale, because of the same difficulty as was encountered by Aitken. The use of the mercury arc for rectifying high potential alternating currents³) at length made possible the employment of power sufficient to meet practical requirements. The development of these ideas and methods to the stage of practical usefulness is due, in great measure, to the labours of F. C. Cottrell.⁴) Since the first installation of his method on a large scale at the Selby Smelter, near San Francisco, in 1907, the process has been widely adopted, not only for the precipitation of lead fume, and gases laden with fine dust of the most varied composition, but also for the clearing of the mists which arise in such industries as the manufacture of sulphuric acid by the oleum process.

In the glow discharge of electricity from points at high potential, particles in the neighbourhood of the points receive an electrical charge and are repelled. If an earthed plate, or one of opposite polarity, be brought near, the particles are attracted, precipitated on the plate, and lose their charges. It has been found by experience that a high, direct-current

¹ Eng. Pat., 1884, 11120.

² W. M. Hutchings, *Berg- und Hüttenmännische Zeit.*, 1885, **44**, 253.

³ O. Lodge, Eng. Pat., 1903, 24305.

⁴ *Smithsonian Report*, 1913. pp. 653—685.

voltage is preferable to an alternating one for the precipitation of dust and fume. The ordinary low-voltage, alternating current generally available is thus transformed, for this purpose, into high-voltage alternating and then into intermittent high-voltage direct current. The last-mentioned operation, known as rectification, may be performed mechanically by the agency of a rotary contact-maker, or by means of vacuum tubes, which allow the current to pass only in one direction.

In the process, as carried out at present, the discharging electrodes, negatively charged by preference, have a voltage of 75,000 to 100,000. They consist of iron chains, carefully insulated, which are hung in the middle of steel pipes 15—20 feet long and 10—18 inches in diameter, through which the gases are drawn. The 'collecting' electrodes, the pipes, are earthed and the precipitated fume is shaken down at intervals by striking them with a hammer. In another form, the discharging electrodes are of light iron wires, the grounded electrodes being made of heavy iron screen. For the efficient working of the process, it is desirable that the temperature, velocity and composition of the gases should be maintained constant.

Electrostatic precipitation of fume from the silver refinery is used at Chrome, N.J. The plant consists of three units, each containing 30 pipes, 30 feet long and 8 inches in diameter, capable of handling 4000 cubic feet a minute. The temperature of the gases is 60—70° and the velocity of flow 7 feet per second. Greater uniformity of temperature is obtained by drawing the gases into the chambers near the top, causing them to pass downwards outside the precipitating pipes, then upwards through the pipes. The chambers are lined with lead, the pipes are made of the same metal and the discharging electrodes are lead-covered iron wires, of star-shaped section. The potential is 65,000 volts. For cleaning purposes, a unit is cut out and the deposited fume removed by flushing.¹)

1 W. G. Smith and A. A. Heimrod, *Chem. Met. Eng.*, 1919, **21**, 360.

At Bunker Hill, only the blast-furnace fume passes to the bag-houses; the remainder is treated in chambers, made of brick, by the Cottrell method. The plant is built in four sections, each containing 64 pipes, and the method of circulation in the precipitating chambers is similar to that employed at Chrome. The fume is detached by hammering the pipes and shaking the chain electrodes, by mechanical means.¹⁾

A Cottrell plant at Trail for the treatment of 100,000 cubic feet of gas per minute consists of 384 pipes. The velocity of the gases for pipes of 12-inch diameter should not exceed 3.5 feet per second.

Fractional precipitation of fume, consisting of materials differing in volatility, is possible by the Cottrell process, when operations are carried out at different temperatures. Thus, high grade white arsenic can be separated from lead fume, by electrical precipitation of lead and zinc compounds at a temperature at which white arsenic is gaseous; on cooling the escaping gases, the oxide of arsenic becomes solid and can be recovered by repeating the electrical treatment.

Gases from reverberatory and blast-roasting plant, which are unsuitable for bag-filtration, owing to the injurious effect of the gases on the cloth, can be treated without difficulty by the Cottrell method.

The treatment of lead-fume and flue-dust generally adopted, is to briquette with lime and clay and add the product to blast furnace charges. It may also form a constituent of blast-roasting charges, though perhaps not very suitable for this purpose. When rich in arsenic it may be profitable or advisable to extract this. The practice at Freiberg may be cited in this connexion. When the arsenic-content is below 7 p.c. the dust is briquetted and then added to ore-smelting charges; when between 7 and 15 p.c. it is roasted before briquetting, and when over 15 p.c. it is roasted in order to recover the arsenic and the residue then smelted.

¹ C. T. Rice, *Eng. Min. Journ.*, 1918, **106**, 771.

CHAPTER IX

USES AND PROPERTIES OF LEAD AND ITS ALLOYS

Owing to the demand for soft lead in many industries, and the hardening effect of minute quantities of foreign metals on lead; owing, also, to the need of purifying the metal before desilverising and to the refining action of the desilverisation-process itself, commercial leads are usually of a high degree of purity. The following table of analyses of some commercial leads shows the nature of the chief impurities and the extent to which they are present:

| | Best English lead | Good chemical lead | Ordinary English lead | B.H.P. Australia special market lead | B.H.P. Australia ordinary market lead | Electrolytic lead, Trail, B.C. |
|--------------------------|-------------------------|--------------------------|-----------------------------|--|---|--------------------------------------|
| Lead (by difference) . . | 99'9919 | 99'985 | 99'9655 | 99'9977 | 99'9917 | 99'9861 |
| Copper | 0'0003 | 0'022 | 0'0019 | 0'0003 | 0'0001 | 0'0027 |
| Antimony . . . | 0'004 | 0'033 | 0'0132 | 0'0005 | 0'006 | Nil |
| Arsenic | Nil | trace | Nil | — | — | 0'0025 |
| Bismuth | 0'0005 | 0'001 | 0'0124 | 0'0006 | — | 0'0037 |
| Silver | 0'0003 | 0'002 | 0'0007 | 0'0002 | 0'0012 | 0'001 |
| Iron | 0'0015 | 0'003 | 0'0031 | — | — | 0'0022 |
| Manganese . . . | Nil | — | Nil | — | — | — |
| Nickel | Nil | Trace | Trace | — | — | — |
| Cobalt | Nil | — | Nil | — | — | — |
| Zinc | 0'0015 | 0'001 | 0'0026 | 0'0007 | 0'001 | 0'0018 |
| Cadmium | Nil | — | 0'0026 | — | — | — |
| Tin | Nil | — | Nil | — | — | — |
| | 100 | 100 | 100 | 100 | 100 | 100 |

Lead is largely used in building construction for gutters, spouts and roofing, for the conveyance of gas and water and for chemical manufacture, where resistance to the corrosive action of acids is required. For all of these purposes its pliability and the ease with which it can be moulded and soldered, or united by autogenous welding, are of the greatest service. A great many of its alloys find application in the arts, as will be indicated later.

The old method for making sheet lead was by casting, but the sheets prepared in this way were often defective, by reason of blow-holes and sand-holes, and the uneven thickness of the sheets produced a tendency to buckling and cracking. The invention of rolling dates from 1670 and was strongly opposed at the time.¹) The method of operating is briefly as follows: The lead, cast into a plate, several inches thick, and still hot from the casting, is passed to and fro between massive iron rollers, 8 feet long and 18 inches in diameter, which are worked by engines with reversing gear. The rolling gear stands in the middle of a long low bench, a little wider than the rollers, and the movement of the lead sheet over this is facilitated by wooden rollers, which are let into the bench at intervals of a foot. When the sheet becomes too long for manipulation, it may be cut into smaller sheets for separate treatment, or chalked to prevent adhering, doubled over and rolled again. When thin enough, the edges are trimmed and the sheet wound on to a cylinder at the end of the bench.

Lead piping is made by the process known as squirting, in which hot, but solid, lead is forced by hydraulic pressure through the annular space between a die and a mandrel. The size of the former determines the outside diameter of the pipe, that of the latter, the internal diameter. The lead is contained in a reservoir, the upper part of which fits tightly into a plug which carries the steel die. The mandrel is firmly fixed to the bottom of the reservoir and projects vertically upwards through the die. The cylinder is forced upwards, the lead is moulded into pipe shape in its escape between die and mandrel and the piping caught and wound on a drum.

THE PHYSICAL PROPERTIES OF LEAD

Lead is a bluish-grey metal with a metallic lustre. Like most of the metals it crystallises in the regular system. Octahedral forms are found in nature and are produced during

¹ See: *The New Invention of Mill'd Lead, for Sheathing of Ships against the Worm, better for Sailing, and cheaper above 1 Cent. per Cent, than the old way with Boards*, London, 1691.

the crystallisation of the metal, as in the Pattinson process; they are also displayed, sometimes in combination with the cube, by etching a surface of the metal. The general crystalline structure of the metal is well shown on the surface of pigs of the best market lead, and its readiness to crystallise is seen in the growth of arborescent forms during the electrolysis of lead solutions, or in the replacement of lead from these by means of zinc, as in the formation of the lead tree (*arbor Saturni*).

Cast lead, when etched, shows the ordinary polygonal structure common to homogenous substances. Rolled lead has a finer-grained structure, though it shows but little evidence of the crystal-elongation which might have been expected, presumably owing to the excessive amount of flow which has taken place in the soft metal. Such plastically-deformed metal undergoes a process of annealing, even at the ordinary temperature, rapidly at a somewhat higher temperature, which is accompanied by considerable growth in the size of the crystals and by the development of twin-crystals.¹) Thus the slight increase in mechanical hardening occasioned by rolling is lost in course of time, and old roofing lead is always found to be coarsely crystalline.

The fracture of lead is hackly when cold, columnar when hot; its tenacity is very low and, like all metals, practically vanishes at a temperature only a few degrees below the melting point; it is readily malleable. It is the densest of the common base metals, its sp.gr. being 11.35 at 20°. This may be taken as a mean value, for the determinations of different experimenters differ within fairly wide limits. Lead from radio-active sources is relatively less dense, the values found by Richards and Wadsworth being, at 19.94°, 11.337 for ordinary lead, 11.288 for radio-active lead.²)

The density of molten lead is about 10.64. This depends, naturally, on the temperature; estimations made by weighing

¹ J. A. Ewing and W. Rosenhain, *Trans. Roy. Soc.*, 1900, 195 A. 279.

² *Journ. Amer. Chem. Soc.*, 1916, 38, 221.

quartz spheres in the metal at different temperatures gave the following results¹⁾:

| | | | | | |
|---------------|--------|-------|-------|-------|-------|
| Temp. . . . | 328° | 400° | 600° | 800° | 1000° |
| Sp. Gr. . . . | 10·875 | 10·85 | 10·71 | 10·49 | 10·15 |

The increase in volume on the passage of solid lead at 20° to liquid at the melting point is thus 4·3 p.c. The dependence on temperature is given by the expression: $10·71 - 0·00139(t - 327)$, three experimental values being: $t = 366$, $d = 10·65$; $t = 444$, $d = 10·55$; $t = 522$, $d = 10·44$: these values are lower than those just cited.²⁾

For rough practical purposes, 1 cubic foot of lead weighs 710 lbs. when solid, 664 lbs. when liquid. Since there is an increase of volume on melting, the statement that lead can be liquefied simply by increasing the pressure is probably inaccurate. The comminuted metal can be readily compacted by compression, or simply by agitation under its own pressure.

The melting point of lead is taken as 328° (National Physical Laboratory) or 327·4° (American Bureau of Standards). The temperature of visible ebullition, under atmospheric pressure, is given as 1525°. By determining the loss of lead at different temperatures and plotting the results, the curve is found to change from logarithmic below the boiling point, to linear above, and the boiling point deduced from this is 1555°. ³⁾ Ingold ⁴⁾ determined the vapour-pressure of lead at various temperatures, his results being:

| | | | | | | | | | | |
|------------|------|------|------|------|------|------|------|------|------|------|
| t °C . . . | 920 | 950 | 1000 | 1050 | 1100 | 1150 | 1200 | 1250 | 1300 | 1340 |
| p (mm Hg.) | 0·49 | 0·86 | 1·77 | 3·69 | 4·87 | 12·8 | 23·2 | 37·5 | 62·0 | 90·3 |

From these data and the vapour-pressure of mercury, the boiling-point of lead is calculated, from Ramsay and Young's formula, to be 1619°. Under greatly reduced pressure, there is a difference of 30° in the boiling point, corresponding to an alteration of 45 mm. in the height of the column of

1 P. Pascal and J. Jouniaux, *Compt. rend.*, 1914, **158**, 414.

2 R. Hogness, *Journ. Amer. Chem. Soc.*, 1921, **43**, 1621.

3 O. Ruff. and B. Bergdahl, *Zeitschr. anorg. Chem.*, 1919, **106**, 76.

4 C. K. Ingold, *Journ. Chem. Soc.*, 1922, **122**, 2419.

vapour ¹⁾ and in the vacuum of the cathode light, the boiling point is 1144° when the height of the vapour-column is 70 mm. ²⁾ Under these conditions the metal is distinctly volatile at 335° ³⁾ and it can be separated quantitatively from tin ⁴⁾, which though more easily melted than lead, has a much higher boiling point.

The rate of volatilisation of the two metals *in vacuo* from the negative electrode shows a similar relationship, the values being 75 for lead, 57 for tin, compared with 100 for gold as standard. ⁵⁾ Under ordinary conditions, the volatility of lead is slight in the absence of air, but is increased by the presence of zinc and other volatile metals. In practice, when air has access to the metal, the case is different and, indeed, from a metallurgical point of view, lead is fully entitled to be regarded as a volatile metal. Examples of smelting are on record ⁶⁾, in which most of the lead in the charge has gone into the flues, and consideration has already been given to the various devices whereby this source of loss can be reduced, and the greater part of the lead which leaves the furnace can be recovered. The vapour density of lead agrees with that calculated, assuming the gas to be monatomic. ⁷⁾

Lead is the softest metal in common use, and of all the metals only thallium, calcium, potassium and sodium are softer. It is scratched with the thumb-nail and marks paper. Despite its softness, it can be prepared in the form of a wool, the fibres of which are excessively fine. ⁸⁾ Its hardness on Moh's scale is 1.5; if taken as unity in hardness tests by the Brinel and Sclerometer methods, the values of some of the other common metals are: tin, 2.5, zinc, 6; copper, 8. The

1 F. Krafft, *Ber.*, 1903, **36**, 1690.

2 F. Krafft and P. Lehmann, *Ber.*, 1905, **38**, 253.

3 F. Krafft and L. Bergfeld, *Ber.*, 1905, **38**, 258.

4 E. Tiede and F. Fischer, *Ber.*, 1911, **44**, 1712.

5 W. Crookes, *Proc. Roy. Soc.*, 1891, **50**, 102.

6 C. W. Hixon, *Notes on Lead and Copper Smelting*, 1898, p. 47.

7 Wartenburg, *Zeit. Elektroch.*, 1913, **19**, 484.

8 O. Ohlmann, *Ber.*, 1912, **45**, 2974.

softness of the metal is invaluable for modelling and is only approached by that of Purbeck marble; it has therefore been largely used for artistic purposes.¹⁾

The index of refraction of the metal, determined by Drude's method, is 2.01; the specific heat of the solid is 0.0293 from -192° to 20° , 0.0338 from 20° to 100° ; of the liquid 0.0402 from 380° to 400° ; the latent heat of fusion is 5.369 calories; the coefficient of linear expansion is 0.2955×10^{-4} between 0° and 100° ; the conductivity for heat is 7.9, for electricity, 7.8 compared to silver, 100; the modulus of elasticity is $1.8-10^3$ kilograms per square mm., and the surface tension at $770-780^{\circ}$ is 424.5 dynes per centimetre. Tellurium lowers the surface tension, so that the bead of metal is flattened during cupellation and absorbed by the cupel. This is a source of loss in the cupellation of gold ores containing tellurium.²⁾

The diffusion of liquid lead at 343° has been studied by determining the rate of permeation of radio-active lead into ordinary lead in upright tubes; the mean value is 2.2 grams per day, across an area of 1 square cm.³⁾ At 492° , gold diffuses to the top of a column of liquid lead in 1 day, the diffusivity being 3 (cm.day units); in solid lead at 251° , the value is 0.023. In cylinders 25 c.m. high, at 18° , gold diffused to a height of 7.65 cm. in 4 years, the assay of the first layer, 0.75 mm. thick, nearest the gold, being 1 oz. 6 dwts. of gold per ton, and of the poorest layer 1.5 dwt. per ton.⁴⁾ Later experiments confirm these results, and in one particular case it was found that the diffusion of gold into lead (both solid) could be traced for a distance of 2.4 cm, whereas that of lead into gold did not exceed 0.2 mm.⁵⁾

¹ See in this connexion W. R. Lethaby, *Lead Work: Old and Ornamental and for the most part English*, 1893; *Journ. Soc. Arts.*, 1897, **45**, 452; L. Weaver, *Journ. Soc. Arts.*, 1910, **58**, 1054.

² T. K. Rose, *Trans. Chem. Soc.*, 1893, **62**, 72; *Trans. Inst. Min. Met.*, 1918, **17**, 463.

³ J. Gröih and G. von Hevesy, *Ann. Physik*, 1920, [VI], **63**, 85.

⁴ W. Roberts-Austin, *Phil. Trans.*, 1896, **187 A**, 383; *Proc. Roy. Soc.*, 1900, **67**, 101.

⁵ C. S. van Orstrand and F. P. Dewey. *U. S. Geol. Sur. Prof. Paper*. No. 95, G. 1915.

Colloidal lead can be prepared by forming a direct current arc, or a high frequency, alternating arc between electrodes of the metal in a suitable medium, or by the oscillatory discharge of a Leyden jar under these conditions¹⁾ or by the action of the ultra-violet light from a quartz-glass mercury lamp on the metal, covered with the dispersion medium²⁾; or by reduction of lead chloride in the cold with hydrazine.³⁾ As obtained by Svedberg, in methyl alcohol, it was deep-brown coloured in transmitted light and bluish black in reflected light.

An allotropic form of lead (or possibly more than one) was prepared by Cohen and Helder⁴⁾ by suspending lead in 40 p.c. solution of lead acetate, containing 10 p.c. nitric acid (D. 1.16). In these conditions, the lead becomes wrinkled and denser. Three specimens of density, 11.3415, 11.3129, and 11.3283, were produced in this way from metal of density 11.3299. According to H. Heller this 'grey' lead is rapidly formed in solution of its acetate, if only a little nitric acid be present. H. J. M. Creighton observed the formation of the same allotrope during the electrolysis of nitric acid (D. 1.42) when lead formed the cathode.⁵⁾

When lead is freshly distilled in silica vessels, it is rapidly attacked by water and oxygen, acting together. If, however, the distilled lead be kept some time *in vacuo*, it is much less easily corroded when brought in contact with water and oxygen. This curious behaviour has been accounted for, by assuming that freshly distilled lead is not physically homogeneous, the varieties (allotropes) differing in their solution-pressures.⁶⁾ There are no observations, as yet, which correlate these allotropes with Heller's grey lead; indeed, the very

1 G. Bredig, *Zeit. anorg. Chem.*, 1898, 951; T. Svedberg, *Ber.*, 1905, **38**, 3616, 1906, **39**, 1712.

2 T. Svedberg, *Ber.*, 1909, **42**, 4376.

3 Gutbier, *Zeit. anorg. Chem.*, 1902, **31**, 448.

4 *Zeitsch. phys. Chem.*, 1915, **89**, 733.

5 *J. Amer. Chem. Soc.*, 1915, **37**, 2034.

6 B. Lambert and H. E. Cullis, *Journ. Chem. Soc.*, 1915, **107**, 210.

existence of allotropes has been denied by some authors ¹⁾ and there is no evidence of their existence from measurements of electrolytic potential. ²⁾

THE CHEMICAL PROPERTIES OF LEAD

Speculations concerning the relationship of lead to the products of the radio-active changes of uranium and thorium have stimulated a great deal of interest in the question of the atomic weight of lead. Soddy ³⁾ has pointed out that the older determinations vary considerably. Thus, of 24 values given in Abegg's *Handbuch*, 19 range almost over a unit, viz.: from 206.8 to 207.6. Recent determinations give fairly consistent results for ordinary lead, but the values for lead derived from radio-active minerals vary considerably. A number of these results are given in the following table:—

| Source of lead | Atomic weight | Observer |
|---|------------------|---------------------------|
| 1. Radio-active minerals, Colorado . . . | 207.00 | Richards and Wadsworth |
| 2. " " Australia . . . | 206.34 | |
| 3. Broggerite | 206.12 | |
| 4. Cleveite, Langesund | 206.08 | |
| 5. Uraninite, N. Carolina | 206.46 | Richards and Lambert |
| 6. Pitchblende, Joachimsthal | 206.57 | |
| 7. Carnotite, Colorado | 206.59 | |
| 8. Thorianite, Ceylon | 206.82 | |
| 9. Pitchblende, England | 206.86 | |
| 10. Ordinary lead (control) | 207.15 | de Coninck and Gerard |
| 11. Uranium mineral | 206.98 | |
| 12. Ordinary lead (control) | 206.71 | |
| 13. Uranium mineral | 206.36 to 206.64 | Maurice Curie |
| 14. Monazite | 207.08 | |
| 15. Ordinary lead (control) | 207.01 | |
| 16. Thorium mineral $\left\{ \begin{array}{l} \text{ThO}_2 \text{ 62 p.c.} \\ \text{U}_3\text{O}_8 \text{ 1.9 " } \\ \text{PbO 0.39 " } \end{array} \right\}$. . . | 208.4 | Soddy |

1 A. Thiel, *Ber.*, 1920, **53**, 1052, 1066.

2 E. Cohen and K. Inouye, *Zeitsch. phys. Chem.*, 1910, **74**, 202.

3 F. Soddy, *Journ. Chem. Soc.*, 1911, **99**, 82; 1914, **105**, 1402.

| Source of lead | Atomic weight | Observer |
|---|---------------|---------------------------------|
| 17. Pitchblende | 206.736 | Hönigschmid and St. Horovitz |
| 18. Pitchblende, Joachimsthal | 206.405 | |
| 19. Uranium mineral, East Africa (formerly German) | 206.046 | |
| 20. Bröggerite $\left\{ \begin{array}{l} \text{U}_8\text{O}_8 \text{ 79 p. c.} \\ \text{ThO}_2 \text{ 4.5 " } \\ \text{PbO} \text{ 9.5 " } \end{array} \right\}$ Norway | 206.063 | |
| 21. Ordinary lead (control) | 207.180 | Davis |
| 22. Samarskite | 206.30 | |
| 23. Thorianite, Ceylon | 206.88—207.24 | Hönigschmid |
| 24. Thorite, Norway | 207.88—207.92 | |
| 25. Spring water, Japan | 207.13 | Richards and Sameshima |

The association in nature of lead and uranium appears to have been first recognised by Hillebrand. A little later, Boltwood,¹⁾ in investigating this subject, determined the ratio of lead to uranium in 43 minerals, and showed that this ratio was constant for minerals of the same geological age. "It is apparent" he said, "that the requirements for a disintegration-product of uranium are fulfilled by lead, within the limits of probable experimental error. On the basis of this evidence, it would appear to be justified that lead is the final product of uranium."²⁾

The study of the radioactivity of uranium has led to the conclusion that the disintegration of one atom of uranium, down to the stage where radium is produced, is attended by the loss of 3 alpha-particles and 2 beta-particles, and the completion of the disintegration-process results in the production of Radium-G., isotopic with lead, and is accompanied by the loss of 5 additional alpha-particles and 4 beta-particles. These relationships allow of the calculation of the atomic weight of Radium-G., from those of uranium or radium, since the alpha-particle is identical with the helium atom (atomic weight 4), and the mass of the beta-particle is negligible, for practical purposes. Taking the atomic weight of uranium as

¹ B. B. Boltwood, *Phil. Mag.*, 1905, IX., 616.

² *Amer. Journ. Soc.*, 1907, XXIII, 77.

238.2 and that of radium as 226, the values calculated for Radium-G. are thus 206.2 and 206.0.

The atomic weight of lead, isolated from various uranium minerals, has been found to approximate closely to 206, (Nos 3, 4, 19 and 20 in the above table); such lead resembles ordinary lead in all chemical respects.

The direct proof of the accumulation of lead in minerals, as the result of the disintegration of uranium or radium, has not been obtained, and is hardly to be expected, since the rate of production is excessively small. From various data it can be deduced that 1 gram of uranium, in 1 year, yields 1.25×10^{-10} gram of Radium-G.; or, assuming that the disintegrating element is constantly replenished, so that 1 gram is always present, then the production of the equivalent of Radium-G. would require 8000 million years. In minerals which are stable, and of primary origin, and concerning which geological and petrological evidence indicates the absence of initial contamination with ordinary lead, and of loss of constituents by weathering, the determination of the ratio Pb/U enables an estimate of their age to be made. This method has been applied by Holmes¹), who ascribes, for example, 1000 million years to certain Norwegian minerals of middle Pre-Cambrian age, in which the ratio Pb/U is 0.013 (mean). The lead isolated from one of these minerals, in which $\text{Pb/U} = 0.013$, was found to have the atomic weight 206.06.

The constancy of the ratio Pb/U in minerals of the same geological age, its variation in those of different ages, and the close approximation of the atomic weight of the lead with that deduced from the disintegration-hypothesis, are strong evidence of the accumulation of lead in minerals, at the expense of uranium, during geological epochs.

The genetic relations between thorium and lead have proved more difficult to establish. The disintegration of

¹ A. Holmes, *Proc. Roy. Soc.*, 1914, A, 85, 248; *Proc. Geol. Ass.* 1915, 26, Pt. 5; 289; *The Age of the Earth*, 1913. R. W. Lawson, *Die Naturwissenschaften*, 1914, Heft 26—27.

thorium results in the end-product, Thorium-D, isotopic with lead, by the loss of 6 alpha-particles (and 4 beta-particles), and the atomic weight of Thorium-D should thus be $232 - 24 = 208$. That this is stable is evident by the isolation of lead from thorite (Sabaragamuwa, Ceylon) by Soddy, the determination of the atomic weight of which gave the value 207.74; this value was confirmed by Hönigschmid.

Opinions differ as to the cause of the variable atomic weights between these extremes, approximately 206 and 208, of the lead derived from radioactive sources. Such leads may be mixtures of ordinary lead and lead isotopes, or ordinary lead may be a distinct variety, or a balanced mixture of the isotopes derived from uranium and thorium, or finally it may be an evolutionary product from lighter materials.¹⁾ Attempts²⁾ to separate ordinary lead into isotopes by centrifugalising the molten metal did not meet with success.

The melting points of two varieties of lead, differing by 0.8 in atomic weight, were found to agree within 0.05° and the Seebeck thermoelectric effect at their junction to be zero.³⁾ The index of refraction and the solubility of the nitrates derived from test lead and lead of atomic weight 206.42 were practically identical.⁴⁾ Richards and Wadsworth, however, found the density of ordinary lead at 20° to be considerably higher (11.377) than that of lead extracted from Australian radioactive minerals (11.288); as the atomic weights vary proportionately to the densities, the atomic volumes are identical, viz.: 18.277 and 18.276. It is evident that the isotopes only differ from one another in respect to mass.⁵⁾

1 F. W. Clarke, *Proc. Nat. Acad. Sci.*, 1918, **4**, 181.

2 J. Joly and J. H. J. Poole, *Phil. Mag.*, 1920, vi., **39**, 372.

3 T. W. Richards and N. F. Hall, *Journ. Amer. Chem. Soc.*, 1920, **42**, 1550.

4 T. W. Richards and W. C. Scumb, *Journ. Amer. Chem. Soc.*, 1908, **40**, 1403.

5 T. W. Richards, *Science*, 1910, 1; *Nature*, 1919, **103**, 74, 93. See, however, Dillon, Clarke and Hinchy, *Sci. Proc. Roy. Dublin. Soc.*, 1922, **17**, 53.

Many of the methods by which lead is obtained from its compounds have been already dealt with, since they are employed technically in the extraction of the metal. Some others, more suitable for laboratory operations, may be recorded here. A quantitative yield of metallic lead can be obtained by the reducing action of stannous chloride on a solution of lead nitrate, made strongly alkaline with 10 p.c. caustic soda.¹⁾

Reactions of replacement of lead by other metals possess some points of interest. Aluminium, copper and mercury are without action on solutions of lead salts; in the case of aluminium, this is probably due to a protective film of oxide, since its amalgam gives an immediate precipitate of lead. Iron replaces lead slowly, zinc and cadmium immediately, from aqueous solutions, but zinc does not affect alcoholic solutions of lead acetate. Tin replaces lead from acetate solutions, but lead replaces tin from nitrate solutions. Combination of chemical and electrolytic precipitation of lead occurs when sheets of zinc and copper, joined in air by a copper wire, are dipped into a solution of lead salt; each metal then acquires a deposit of lead upon it, the zinc rapidly, the copper slowly. In the reaction between zinc and lead nitrate solution, the quantity of metal deposited is trebled as the concentration of the solution is doubled.²⁾

Hydrogen, too, is able to replace lead, though the effect is only observable at high gaseous pressures and at a moderately elevated temperature. In the case of lead nitrate, basic salts are produced, but with lead acetate in tenth normal solution, at a temperature of 240° and a pressure rising to a maximum of 242 atmospheres, complete separation of lead in crystalline form has been observed.)

Of the many methods of preparing lead of the highest degree of purity, suitable for atomic weight determination

1 L. Vanino and F. Treubert, *Ber.*, 1898, **31**, 1118.

2 J. H. Gladstone and A. Tribe, *Proc. Roy. Soc.*, 1871, **19**, 498.

3 W. Ipatiew and W. Werchowsky, *Ber.*, 1909, **42**, 2078.

and similar work, that of Stas may be cited.¹⁾ Solution of lead acetate is digested at 40—50° with lead foil, in order to precipitate copper and silver. The liquor is filtered into sulphuric acid, the lead sulphate washed and dissolved in ammonium carbonate solution, made strongly alkaline with ammonia; the carbonate thus formed is washed free from ammonium salts and the removal of iron, the chief impurity, effected in the following way. Part of the carbonate is converted into oxide by gently heating in a platinum dish, the remainder is converted into neutral nitrate, this dissolved in boiling water and the oxide added to the solution in small portions at a time. Iron is thus precipitated and the solution of basic nitrate, filtered into ammonium carbonate, gives a precipitate of pure lead carbonate. This is washed and dried and reduced to lead by adding it to molten potassium cyanide contained in an unglazed porcelain crucible. The button is melted again under cyanide and when pure appears convex and like quicksilver; a trace of litharge or lead sulphate destroys the convexity of the surface. Alternative methods are: to reduce the carbonate with black flux (from pure Seignette salt), dross the lead until alkali is removed and melt under cyanide; to dissolve the carbonate in hydrochloric acid, filter off the soluble iron and reduce the chloride by fusing with a mixture of sodium carbonate and potassium cyanide, or by means of black flux as before.

The metal is cast in polished steel moulds; when thus purified, it is much whiter and softer than ordinary lead and is very quickly oxidised by air.

Lead in a finely divided state, such as that produced by the decomposition of lead tartrate, is pyrophoric. Even when granulated, it absorbs atmospheric oxygen readily, especially in contact with water, and its application as an absorbent for oxygen in gas-analysis was long ago suggested by de Saussure.²⁾ In the hands of Schönbein, its use led to the

1 J. S. Stas, *Recherches sur les rapports réciproques des poids atomiques*.

2 Ann. Chim. Phys., 1836, 62, 219.

recognition of the phenomenon of autoxidation, for he found that 1 gram of lead and 300 grams of mercury, when shaken in presence of oxygen with 300 c.c. of dilute sulphuric acid, yielded hydrogen peroxide equivalent in amount to the lead oxidised and fixed as sulphate, the quantities of active oxygen and bound oxygen being respectively 1.39 and 1.46 mgm.

The action of atmospheric agents, water, oxygen and carbon dioxide, and of natural waters containing the two gases, upon lead has been the subject of continuous study for a century or more, chiefly on account of its importance in connexion with the conduction of supplies of water for domestic purposes. Though tolerable agreement has been reached on issues of practical importance, there is much diversity of opinion on many points of fundamental chemical interest.

Lead of a high degree of purity, distilled in quartz vessels, is stated by Lambert and Cullis¹⁾ to be unaffected by pure water. It is maintained by some²⁾ that, though no chemical action takes place, the metal passes into the colloidal state, in which it is particularly susceptible to oxidation. The combined action of water and oxygen is rapid, the ultimate result being the production of oxide, and possibly suboxide, of lead, which may be hydrated and are partly crystallised; as an intermediate stage, there is the possibility of the formation of colloidal materials, of like composition, which become slowly aggregated. These oxide-bodies are soluble in water to the extent of 20 mgm. of lead per 100 c.c.³⁾, the evidence of solubility, given long ago by Col. Yorke⁴⁾, being: that indicator-tests show the presence of an alkali; that length of subsidence does not affect the lead-content, and that electrolysis gives a deposit of lead at the cathode and lead peroxide at the anode. The same author found that the lead in

1 *Journ. Chem. Soc.*, 1915, **107**, 210.

2 Manganini and Scala, *Mem. R. Accad. Lincei.*, 1911, **8**, 376; W. Heap, *Journ. Soc. Chem. Ind.*, 1913, **32**, 771, 811, 847.

3 J. C. Thresh, *Analyst*, 1921, **46**, 270.

4 P. Yorke, *Phil. Mag.*, 1834, 3rd. Series, **5**, 81; 1846, **28**, 17.

this solution is adsorbed by filter paper and this evidence of its colloidal nature is confirmed by Thresh's observation (*op. cit.*), that it will not pass through a Pasteur filter.

When carbon dioxide is present, it is absorbed rapidly by the lead base, the alkalinity of the solution disappears and there is deposited a crystalline precipitate of a basic carbonate, of the formula $3\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$.¹⁾ This falls away from the surface of the lead, with the result that more metal becomes oxidised and the formation of the carbonate takes place continuously. Under the combined action of ordinary air and pure water, the lead is thus very speedily corroded.

Natural waters contain salts in solution, some of which, by causing the deposition of a firm, coherent crust of insoluble compounds on the surface of the lead, protect the metal from corroding agencies and render safe its conduction through lead pipes. The phosphates, carbonates and bicarbonates of calcium and sodium are the most efficacious in this respect, and close to them stand the sulphates and chlorides. Calcium bicarbonate, present to the extent of 1 part in 50,000 of water, affords a protective covering to the metal, and lime inhibits its corrosion when in quantities of the order 1 in 10,000; in larger amount than this it facilitates the solution of the lead. Some experimenters ascribe to small quantities of silicates an important part in the prevention of corrosion of lead; all are agreed that nitrates, especially the nitrate of ammonium, which indicates the past pollution of water, facilitate very much the solvent action of water on lead.

Peaty waters, especially those which are soft, are liable to dissolve lead and should be treated with limestone in order to render them safe. In the neighbourhood of large towns, a soft water is apt to become acid, from absorption of sulphuric acid. This increases its solvent action, even when present to the extent of only 1 part per million.²⁾ Cases of

1 F. Clowes, *Proc. Chem. Soc.*, 1902, No. 247.

2 W. C. Williams, *Journ. Soc. Chem. Ind.*, 1887, 6, 111.

lead-poisoning by water in Sheffield and Huddersfield have been traced to the acidity of the water.

Since air facilitates the solvent action of water, an intermittent water supply is favourable to the contamination of the water, and as lengthened contact with lead, in the case of an active water, will naturally result in a considerable proportion of the metal being dissolved, it is advisable to run off the water that has been standing over night in the pipes, as such water may be unfitted for drinking purposes.

The action of sea-water on lead is exemplified in the case of the fireship, *Firebrand*, burnt and sunk in Falmouth Harbour in 1780, raised in 1846. The lead from the pump had been melted and was mixed with charcoal; in the cavities of the metal were found crystals of galena, cotunnite, anglesite, and leadhillite.¹⁾

Lead piping is corroded on the outside when bedded in ashes, lime mortar or Portland cement, but not in clay. Analysis of a corroded lead coffin, 80 years old, gave, according to Pepper, $\text{PbO} = 82.29$, $\text{CO}_2 = 15.15$, $\text{H}_2\text{O} = 0.10$, $\text{Fe}_2\text{O}_3 = 1.94$, Loss = 0.52, which shows it to be a slightly basic carbonate (pure lead carbonate requires $\text{PbO} = 83.52$, $\text{CO}_2 = 16.48$ p.c.). Old Roman coffins are often embedded in coal, but it is doubtful whether this has any chemical significance.

Certain soils, like those of Western Canada, corrode lead with great ease, cavities or wort-like excrescences being formed, and the lead converted into carbonate, sulphate, or yellow, red, and black oxides. Analyses show these soils to be rich in limestone meal and to abound in salts soluble in water, such as sulphates, bicarbonates and chlorides of magnesium, calcium and sodium. Shipley²⁾ attributes the formation of the higher oxides of lead to the production of hydrogen peroxide in the reaction between lead, water and oxygen, and the rapid corrosion to electrolytic action dependent on the different electrolytic solution-pressures of the

1 A. Russell, *Min. Mag.*, 1920, **19**, 64.

2 J. W. Shipley, *Journ. Soc. Chem. Ind.*, 1922, **41**, 314 I.

lead allotropes. Stenger¹⁾ thinks that the formation of concentration-cells, occasioned by the varying concentration of the salt solutions in contact with the lead, may play an important part in its destruction. The perishing of the metal, or the loss of its malleable properties, is referred by Rawdon²⁾ to electrolytic dissolution of its intergranular impurities, with resulting isolation of the crystallites; this effect is particularly noticeable when lead piping is bent, and thus under strain, and its magnitude is apparently proportional to the degree of straining. It is the process termed by Thiel 'disglomeration' and held by him to account satisfactorily for many phenomena, explained by others on the assumption of the existence of allotropes of lead.³⁾

There are some interesting observations on the corrosion of roofing lead. According to Watson⁴⁾ the crust is best developed on the under surface of the south side of the roof and in quality is "as good as the best white lead"; the corrosion is brought about by vapours from the wood (in conjunction with air) and oak has a stronger action than ash. These observations have been confirmed in recent times. Brame⁵⁾ found sheets of lead, 100 years old, perforated in contact with oak, and the crust had the composition of white lead. Southerden⁶⁾ states that the roofing of Axminster church, laid on deal in 1833, was sound after 85 years, whereas the portion laid on oak in 1909 was thickly encrusted after 9 years. It is possible that the corroding agent in these cases is acetic acid, and if that be so, the scale is really white lead.

The best solvent for lead is dilute nitric acid; the action of the concentrated acid is soon arrested by the formation of a protective layer of lead nitrate on the surface of the metal. The action of hydrofluoric acid is likewise checked,

1 L. A. Stenger, *Chem. Met. Eng.*, 1920, **22**, 965.

2 H. S. Rawdon, U. S. *Bureau of Standards*, Bull. No. 377, 1920.

3 A. Thiel, *Ber.*, 1920, **53**, 1052.

4 *Chemical Essays*, 1789, Bk. 3, No. 10.

5 J. S. S. Brame, *Journ. Soc. Chem. Ind.*, 1918, **37**, 39.

6 F. Southerden, *ibid.*, 85.

owing to the insolubility of the lead fluoride initially produced. Hydrochloric and sulphuric acids, when dilute, do not attack lead, but the concentrated acids dissolve the metal at their boiling temperature.

As lead is so largely used in the construction of chambers for making sulphuric acid, its resistance against corrosion by nitrous sulphuric acid is of great importance. Opinions have varied a good deal, as to the influence of the addition of small quantities of other metals on the resistance of the lead to corrosion by these acids. Comparative tests with rolled strips of pure lead and lead alloyed with antimony and copper were made, under working conditions, by hanging them in the chambers for 110 days and determining the resulting loss of metal.¹⁾ The loss in the case of pure lead was 7·5 p.c.; for alloys of varying composition it was found to be:

| Lead-Copper Alloys Copper p.c. | Loss p.c. | Lead-Antimony Alloys Antimony p.c. | Loss p.c. |
|---|--------------|---|--------------|
| 0·1 | 7·1 | 0·1 | 8·1 |
| 0·2 | 7·1 | 0·2 | 0·2 |
| 0·3 | 7·5 | 0·3 | 10·9 |
| 0·4 | 9·1 | 0·4 | 11·6 |
| 0·5 | 8·5 | 0·5 | 11·8 |

From these experiments, antimony appears to be definitely harmful, copper beneficial in amounts up to 0·2 p.c. Laboratory tests on chemical lead, the total impurities in which do not usually exceed 0·02 p.c., have shown that even 0·01 p.c. of antimony makes the lead unfit for chamber use, but 0·06 p.c. restores the metal. Tin and mercury are both harmful, and bismuth also, when present to the extent of 0·04 p.c. When bismuth and antimony are present together, 0·005 p.c. of each, they neutralise each other's bad effects. Copper and sodium are the only metals beneficial in their effects, 0·02 p.c. of copper, for example, neutralising the effect

1) J. Glover, *Trans. Newcastle Chem. Soc.*, 1882, 5, 132.

of 0.05 p.c. of bismuth.¹⁾ Generally speaking, however, pure lead is to be recommended for use in chamber-construction, though as Cookson pointed out, much depends on the physical condition of the metal, for rolling sometimes causes pure lead to fracture.

Lead combines directly with many of the non-metals, e.g. the halogens and members of the oxygen family, but not with nitrogen or carbon. Phosphorus is dissolved in it and converted into a modification, which carries a little lead, known as Hittorf's Phosphorus. This is prepared by heating lead and phosphorus, in the proportion of 100 to 3 by weight, in sealed tubes of Jena glass, for 2—8 days at 800° C. The lead is afterwards separated by electrolysis in a bath of lead acetate solution; the yield of the phosphorous modification is 1 gram per 200 grams of lead.²⁾

Silicon dissolves in lead (as it does also in tin, zinc, silver and aluminium) but to an extent which is barely appreciable at 1100° and attains a value only of 0.78 p.c. at the boiling point of the metal. The relationship between temperature and solubility is shown in the appended diagram³⁾ (Fig. 34):

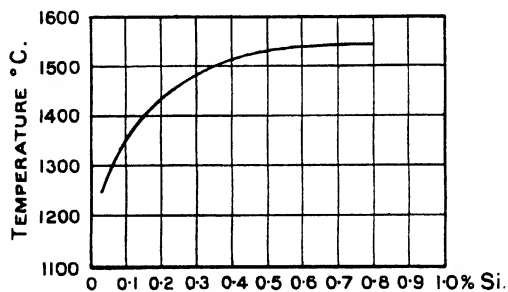


Fig. 34—Solubility of Silicon in Lead.

THE ALLOYS OF LEAD

The impurities usually encountered in work-lead have the effect of hardening the metal, and the processes whereby they

1 D. W. Jones, *Journ. Soc. Chem. Ind.*, 1920, **39**, 221 T.

2 A. Stock and F. Gomolka, *Ber.*, 1909, **42**, 4513.

3 H. Moissan and F. Siemens, *Ber.*, 1905, **38**, 2086.

are removed are known as softening processes, and as such have already been described. Most of the alloys of lead are made from pure lead, by melting it with a suitable quantity of the alloying metal. There is one important exception in the case of lead-antimony alloys, which are often produced directly in blast furnace practice, by the smelting of scums, etc. from the softening furnaces.

In respect to their behaviour towards lead, the other metals display wide differences. Aluminium and lead, for example, appear to be quite insoluble in one another, even at a high temperature; tungsten dissolves in lead to the extent of 30 p.c. at 1300°¹); but is completely rejected from solution on cooling; silver is completely soluble in all proportions in the liquid state, and the pure metals separate on solidification; the solids deposited on the freezing of lead-tin alloys are solid solutions of one metal in the other; finally, definite compounds are formed in solutions of lead and gold. In the account which follows, the more important of the binary alloys will be first considered, and then a few of the more complex alloys containing three or more constituents.

Silver-Lead alloys. The solids, which crystallise from systems of silver and lead, are the pure metals themselves and their eutectic, which freezes at 303° and contains 2.25 p.c. of silver and 97.75 p.c. of lead. The importance of this behaviour in connexion with the Pattinson desilverising process has already been described (p. 152). Bullion-leads exhibit segregation of silver, which has an important bearing on sampling. A cast bar is richer in silver at the outer, more-quickly cooled edges than inside, the assay-differences on a 258 oz. lead being as much as 20 ozs. of silver per ton.²)

Bismuth-Lead alloys. Solid solutions, containing 10 p.c. of lead in bismuth and 10 p.c. of bismuth in lead³), are de-

1 S. Inouye, *Mem. Coll. Sci., Kyoto*, 1920, 4, 43.

2 L. S. Austin, *The Metallurgy of the Common Metals*, 1913, p. 68. For methods of sampling see Hofman, *Metallurgy of Lead*, p. 383.

3 According to Di Capua bismuth dissolves 4 p.c. of lead, and lead 34 p.c. of bismuth in the solid state; the latter value is probably too high. *Atti R. Accad. Lincei*, 1922, [V] 31, 162.

posited from these alloys and an eutectic is formed which freezes at 125° and contains 56 p.c. of bismuth and 44 p.c. of lead. The bearing of these facts on the Pattinson process has been indicated on p. 161.

Cadmium-Lead alloys. These belong to the simple eutectiferous series of alloys, with an eutectic freezing at 249° and containing 20 p.c. of cadmium and 80 p.c. of lead. The solid solubility of each metal, with respect to the other, is zero (Di Capua, *op. cit.*).

Antimony-Lead alloys. The equilibrium-diagram of these important alloys is shown in Fig. 35. The eutectic freezes at

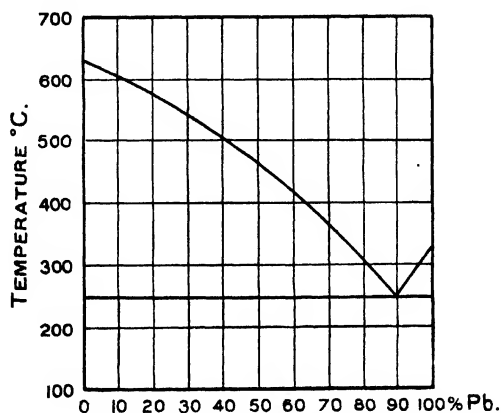


Fig. 35.—Equilibrium-Diagram of Alloys of Antimony and Lead.

248° and contains 12.5 p.c. of antimony and 87.5 p.c. of lead: no solid solutions are formed. Alloys containing more than 12.5 p.c. of antimony thus consist of crystallites of that metal, surrounded by eutectic, and on polishing, the former stand out in relief, by reason of their greater hardness. The hardness of the alloys increases uniformly up to the eutectic composition, then rises rapidly up to 75 p.c. of antimony and falls from that point with increasing antimony content. The expansion on solidification is a maximum at the eutectic composition.¹⁾

¹ D. Ewen, *Journ. Inst. Metals*, 1910, 4, 130

Lead bullets and accumulator plates contain 5 p.c. of antimony, regulus metal for acid cocks and pumps, 10—15 p.c. of antimony. Type metal, the requisites for which are that it should be easily melted, should fill the moulds sharply, be hard enough to resist bending and soft enough not to cut paper, contains 10—25 p.c. antimony; to correct the hardness of the richer alloys, tin is usually added, and occasionally copper. Analyses of such alloys show: 1. Pb = 50, Sb = 25, Sn = 25; 2. Pb = 60, Sb = 30, Sn = 10; 3. Pb = 70, Sb = 18, Sn = 10, Cu = 2 p.c.

Bearing metals often contain 12—20 p.c. antimony. Such alloys must contain hard particles, to resist wear and carry the load, and a soft matrix to supply the necessary plasticity and to secure adjustment. Tin and copper are often added to these anti-friction alloys; examples are 1. Pb = 70, Sb = 15, Sn = 15; 2. Pb = 80, Sb = 15, Sn = 5 (Magnolia metal); 3. Pb = 80, Sb = 10, Cu = 10 p.c.

Antimony-lead alloys are sonorous; they are shattered when struck warm. They show a great tendency towards the floatation of the antimony crystals and so require to be cooled quickly in order to ensure the uniform distribution of the antimony. The segregation of antimony is observable even with alloys of eutectic composition, and leads, as in the case of silver, to difficulty in sampling, as the tops of the ingots are richer in antimony than the bottoms. Test samples examined by Duncan from an ingot of antimonial lead, three chippings being taken from the top and three from corresponding places at the bottom, gave the following results (antimony p.c.):—

| | I. | II. | III. |
|------------------|------|------|------|
| Top | 20·3 | 21·9 | 19·4 |
| Bottom | 13·5 | 11·3 | 13·6 |

The average of these six assays is 16·6 p.c. A dipped sample, taken from this ingot after melting, was cast in a mould $2\frac{1}{2}$ by $1\frac{1}{2}$ by $\frac{3}{16}$ inches and sawn through the middle: the

sawings assayed 15.6 p.c. antimony. This method of taking small dipped samples has been proved to be accurate, by comparison with samples taken directly from the furnace before casting, and by melting lead and antimony in known proportions and comparing the dipping assays with the known composition of the alloy.¹)

Arsenic-Lead alloys show an eutectic, freezing about 290° and containing 3 p.c. of arsenic and 97 p.c. of lead. The chief industrial use of these is in the manufacture of lead shot. For this purpose, the lead is alloyed with a small quantity of arsenic, 0.3—0.8 p.c., which is added either in the form of white arsenic, or arsenical dross from the improving furnace. The addition of arsenic imparts greater fluidity to the metal and increases the tendency of the metal to assume a spherical form in passing through the air. With too little arsenic, the drops are either cupped (hollow in the middle) or pear-shaped; with too much, the shape is double convex. The molten metal is made to run through cullenders, hollow, perforated hemispheres, about 10 inches in diameter and to fall from a considerable height into water-butts. A small amount of sodium sulphide (about 0.025 p.c.) is added to the water to prevent oxidation of the lead. The height required for the fall is either secured by means of a shot tower, or by a deep well, the shaft of an old coal pit being in some cases adapted for this purpose. The size of the shot is determined by the size of the holes in the cullender, by the height from which the lead falls, and by the temperature and consequent fluidity of the molten metal. Shot is sorted by sieving and the imperfect ones separated by causing the shot to roll down an inclined polished surface, sloping at 15° . The perfect shot acquire the highest velocity and shoot well over the edge of the table into a bin; the imperfect ones fall short of this and are gathered apart. The shot is finally polished with graphite in a revolving cask.

Tin-Lead alloys are characterised by an eutectic temperature of 183° and a corresponding composition, $\text{Sn} = 63$,

¹ J. B. Duncan, *The Vasculum*, 1921, 7, 76.

Pb = 37 p.c. Alloys richer in tin than this deposit pure tin; on the other side of the eutectic, solid solutions of tin in lead are thrown down on cooling, which contain about 16 p.c. of tin at the eutectic temperature. The solid solubility falls off with decreasing temperature, being 14.5 p.c. at 175°, 10 p.c. at 150°, 6.5 p.c. at 100° and only 1.5 p.c. at 25°.¹) Thermal effects, due to the transition of rhombic to tetragonal tin, are observed in cooling alloys containing structurally-free tin.

The chief commercial alloys of tin and lead are solder and pewter. One of the solders used by the Romans, *tertium*, has practically the composition of the eutectic mixture, and has thus the lowest possible melting point. A sample unearthed at Silchester, dating from about 300 A.D. was found by Gowland²) to contain Pb = 61.93, Sn = 28.01 p.c. The same alloy is now known as *Tinman's Solder*; it is said to be improved by the addition of 2 p.c. of antimony and a little copper.³) The Roman *'argenterium'*, containing equal weights of each metal, is the common solder of modern use, and coarse or plumber's solder contains Pb = 67, Sn = 33 p.c. The latter has a range of solidification of about 70° and, passing through a pasty stage during this interval between complete liquidity and complete solidity, is used in making wiped joints. When plumber's solder is drossed, it yields an oxide, putty powder (*potée d'étain*), containing about 30 p.c. SnO₂ and 70 p.c. PbO, which is used for polishing and in the making of enamels.

Pewter or Latten Ware (Fr.: *Laiton*, brass, tin-plate) came into use in the fifteenth century. In 1640, King Charles, hearing of the discovery of tin in Barbary, and fearing loss of revenue from the mines in Cornwall and Devonshire, forbade the importation of tin, and directed all measures for wine and ale to be made of tin or pewter and stamped. This custom has survived to the present day. Owing to the risk of lead-poisoning in the use of this alloy, the proportion of

1 N. Parravano and A. Scortecchi, *Gazzetta*, 1920, **50**, 1, 53.

2 *The Metallurgy of the non-ferrous Metals*, 1914, p. 68.

3 C. O. Bannister and H. J. Tabor, *Journ. Inst. Met.*, 1909, **2**, 85.

lead is kept low, being 20 p.c. in England; in France the legal limit is 18 p.c. of lead.

Terne plates are thin sheets of steel coated with an alloy of tin and lead: (Pb = 75, Sn = 25 p.c.); they are employed in Lancashire for packing dry goods, and in America for roofing. A cheaper substitute for terne plates is made by coating iron with antimony and depositing lead over this.¹⁾

Zinc-Lead alloys. The chief characteristic of the systems composed of zinc and lead is the limited mutual solubility of the components. Conjugate alloys are thus produced, and these separate by gravity, the lower one being lead saturated with zinc, the upper, zinc saturated with lead. The important bearing of these relations in connexion with Parkes' desilverising process has already been noted. With rise of temperature, the solubility of each metal in the other increases, until at the critical temperature of solution, the solubilities are identical. This happens at a temperature, estimated indirectly, as 935°; the system then contains 58 p.c. of zinc and 42 p.c. of lead. Zinc and lead also form an eutectic containing 1.5 p.c. of zinc, which freezes at 317°, that is 10° lower than pure lead.

Copper-Lead alloys. The equilibrium-diagram of these alloys is shown in Fig. 36.

There is an eutectic point, which cannot be shown in the figure, corresponding to the composition, Pb = 99.94 p.c., Cu = 0.6 p.c. and a temperature 327°, only one degree below the melting point of pure lead. The liquidus rises steeply from this point and becomes horizontal at 975°²⁾, the conjugate solutions then containing about 15 and 60 p.c. of copper; the dotted lines are probable curves of liquid solubility. All alloys between these limits of composition thus separate into two layers and, on cooling, the upper layer deposits copper at constant temperature, until the liquors from it contain 15 p.c. of that metal. These are partly enmeshed by the crystals of copper, and partly sink

1 C. Baskerville, *Journ. Ind. Eng. Chem.*, 1920, **12** (2), 152.

2 Bogitsch, *Compt. rend.*, 1915, **161**, 416

to the lower layer. Below 975° , crystallisation of copper from the 15 p.c. liquor takes place, and proceeds until the eutectic composition is reached. The lighter crystals of copper tend to float. This system affords a good example of limited liquid solubility and the nearness of the eutectic point to the lead boundary, coupled with the steep rise of the liquidus from this point, are factors of great importance in the softening of lead contaminated with copper. Other examples of partial

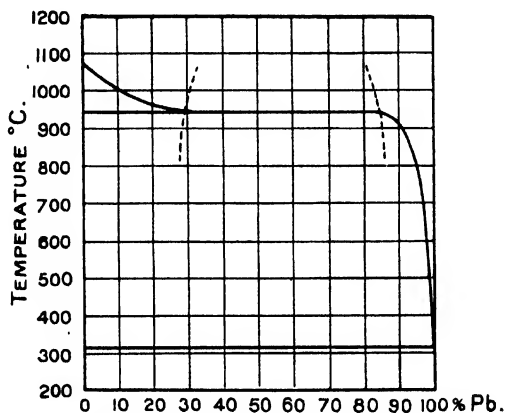


Fig. 36.—Equilibrium Diagram of Alloys of Copper and Lead.

miscibility are met with in the alloys of lead with manganese, nickel, cobalt and iron; in the case last mentioned, the solubility is so small that slowly-cooled lead seldom contains more than 0.0015 p.c. of iron.

Gold-Lead alloys form an eutectic freezing at 215° , of the composition $\text{Au} = 15$, $\text{Pb} = 85$ p.c. and two compounds Au_2Pb and AuPb_2 . Those which are poor in gold thus behave like the alloys of silver and lead on pattinsonising. With the advent of zinc into the system, however, important differences are established; these have been noted in the description of Parkes' process.

Other metals which combine with lead, adding thereby complexity to the equilibrium diagrams are sodium, potassium,

platinum and palladium. In the case of sodium, for example, no less than four compounds are stated to occur, Na_4Pb , Na_3Pb , NaPb , Na_2Pb_3 . It is owing to the formation of one (or more) of these that a solution of sodium in liquid ammonia can dissolve lead.¹⁾ Some of these alloys are very reactive, in the sense that their constituents suffer oxidation with great ease. Examples of this are the alloys of lead with sodium, thallium and magnesium. Magnesium-lead alloys containing 5—50 p.c. of magnesium, and of these especially the one with 10 p.c. of that metal, absorb the oxygen in moist air completely, yielding a black powder containing magnesium hydroxide and (hydrated) sub-oxide of lead. The latter is oxidised in time to the monoxide stage. At 150°, the lead is completely oxidised to litharge and hydrogen is evolved.²⁾

The *Ternary* and *Quaternary* alloys present great difficulty in their investigation; technically, however, they are of considerable importance. It will suffice to quote the ascertained data in one particular example³⁾, namely, in that of the *tin-bismuth-lead* alloys. The melting points of the individual metals are: tin, 232°; bismuth, 269°; lead 328°. All the metals are completely soluble in one another when molten, partly soluble when solid. There are three binary eutectics, the characteristics of the invariant systems being:

| | Freezing point | Composition |
|-------------------|----------------|----------------------|
| Tin-lead | 183° | Sn = 63 Pb = 37 p.c. |
| Tin-bismuth . . . | 124° | Sn = 44 Bi = 56 .. |
| Bismuth-lead . . | 136° | Bi = 57 Pb = 43 .. |

The solid solubility of these metals in each other at the respective eutectic temperatures is:

1 F. H. Smyth, *Journ. Amer. Chem. Soc.*, 1917, **39**, 1290.

2 E. A. Ashcroft, *Trans. Faraday Soc.*, 1919, **14**, 271.

3 G. H. Gulliver, *Metallur. Alloys: their Structure and Constitution*, 1921, p. 355.

| | Solid-solubility | | | |
|---------------|------------------|------|-----------------|------|
| | | p.c. | | p.c. |
| Tin-lead . . | tin in lead | 16 | lead in tin | 0 |
| Tin-bismuth . | tin in bismuth | 1.5 | bismuth in tin | 9.5 |
| Bismuth-lead. | bismuth in lead | 5 | lead in bismuth | 4 |

Finally, there is a ternary eutectic, freezing point 94° ; composition Sn=16, Bi=52, Pb=32 p.c.

The low freezing points of the ternary alloys of eutectic composition is noteworthy. Many of the technical, fusible alloys belong to this group; some are quaternary, having cadmium (m.p. 320°) as an additional constituent. The composition and melting point of the best known are given below:—

| Fusible Alloys | Composition (in parts by weight) | | | | |
|------------------|----------------------------------|---------|------|---------|---------------|
| | Tin | Bismuth | Lead | Cadmium | Melting point |
| Newton | 3 | 2 | 5 | — | 94.5 |
| Rose | 1 | 2 | 1 | — | 94.0 |
| Lichtenberg . . | 2 | 5 | 3 | — | 91.5 |
| Wood | 1 | 4 | 2 | 1 | 71.0 |
| Lipowitz | 4 | 15 | 8 | 3 | 60.0 |

The *tin-antimony-lead* alloys constitute the bearing metals which have been spoken of in connexion with the binary alloys of antimony and lead. Such alloys should be quickly cooled on casting, to prevent floating of the crystals of solid solution of tin and antimony which first separate.

The *copper-tin-lead* alloys, or plastic bronzes, are also used as bearing metals, the addition of lead to bronze having the effect of diminishing the wear of bearings. Very little of the lead dissolves in the alloy, but the fusibility is increased. Segregation of lead is minimised by quick cooling and sometimes by the addition of a small amount of nickel. Most of the bronzes of antiquity contain lead; the following analyses will show how widespread was the custom of adding lead to bronze:

| Source and Description | Analyses of Ancient Bronzes | | | | | | |
|--|-----------------------------|-------|-------|---------------|------|------|--------|
| | Copper | Tin | Lead | Anti- mony | Zinc | Iron | Total |
| 1. Etruscan Mirrors . | 67.12 | 24.92 | 8.13 | — | — | — | 100.18 |
| 2. Assyrian Bronze . | 83.86 | 8.19 | 7.67 | — | — | 0.27 | 99.99 |
| 3. " " . | 85.07 | 5.33 | 8.48 | — | — | 0.75 | 99.63 |
| 4. Celtic Arrow Head | 70.30 | 24.53 | 5.20 | — | — | — | 100.03 |
| 5. Roman Coin (Justinian) | 84.53 | 6.82 | 8.65 | — | — | — | 100.00 |
| 6. Chinese Money (722 to 481 B.C.) . . . | 46.2 | 9.2 | 43.5 | — | — | — | 100.9 |
| 7. Japanese Temple Bronze | 88.70 | 2.58 | 3.54 | 0.10 | 3.71 | 1.07 | 99.70 |
| 8. Japanese Old Bronze Ornament . | 82.72 | 4.36 | 9.90 | — | 1.86 | 0.55 | 99.39 |
| 9. Japanese Ornament | 71.00 | 5.50 | 20.35 | — | 1.34 | 1.84 | 100.03 |

References: 1, Anal. *Francis*. Quoted in Beckmann, II, 64; 2 & 3; M. Busch, *Zeit. anorg. Chem.*, 1914, **27**, 562; 4 & 5; Roscoe & Schorlemmer, *Metals*, p. 832; 6: M. Chikashige, *Journ. Chem. Soc.*, 1920, **118**, 917; 7, 8, 9: W. Gowland, *Journ. Inst. Metals*, 1910, **5**, 4.

Copper-zinc-lead-alloys. Lead is also added to brass, up to about 5 p.c. in amount, to make the alloy more easily machined. As in the case of bronze, it is easily liquated out, though it dissolves in the solution to some extent and gives the resulting alloy the appearance of containing a different proportion of copper than it actually possesses.

CHAPTER X

COMPOUNDS OF LEAD—THE OXIDES

No less than six oxides of lead have been recognised as individuals, Pb_2O , PbO , Pb_3O_4 , Pb_2O_3 , Pb_6O_8 , and PbO_2 .

Lead Sub-oxide, Pb_2O , is a black velvety powder of sp.gr. 8.342 at 18° which is formed when lead oxalate is heated, in the absence of air, at a temperature below 300°¹), and when litharge is reduced with water-gas at a low temperature. It

¹ F. J. Brislee, *Journ. Chem. Soc.*, 1908, **93**, 154.

is a constituent of the residue left by the decomposition of water by the reactive alloys of magnesium and lead, and is possibly formed by air-oxidation at a low temperature of metallic lead. It is resolved readily into lead and lead monoxide, either by heating, or by the action of alkaline or acid solutions; when dilute acids are used, a salt of lead is formed and metallic lead remains. The formation of the sub-oxide of lead plays an important part in the Bischof method of making white lead, since it can be readily converted by direct hydration and oxidation into the hydrated monoxide which, in turn, is transformed into white lead by simple carbonation.

Lead Monoxide, PbO. The chief varieties of this compound are litharge and massicot, the former name referring, strictly, to the fused, the latter to the unfused compound. The tendency at the present time is to use the term litharge for all varieties of lead monoxide.

It occurs native in Kurdistan as a red, partly crystalline mineral with a yellowish-brown streak: the sp.gr. is 8.61 and analysis shows it to contain: $\text{PbO} = 97.17$; $\text{CuO} = 2.61$; $\text{Sb}_2\text{O}_3 = 0.30$ p.c.¹) It has also been recorded from Austria and California as a yellow mineral, the constituent crystals of which are orthorhombic, biaxial and optically positive, which is surrounded by a fringe of reddish tetragonal crystals, uniaxial and optically negative.²)

It is produced directly from lead, by oxidation, and is thus a by-product of the cupellation-process, or by the action of heat upon the higher oxides and many of the other compounds of lead. It is used in the manufacture of flint glass, as a glaze for earthenware, for the preparation of lead acetate, lead nitrate, lead chromate, lead plaster, for drying oils, for proofing fabrics, and in the manufacture of rubber and electrical accumulators, and is prepared for these purposes by drossing lead in a small reverberatory furnace, the oxide being pushed back, as it is formed, in order to expose a fresh surface

¹ A. Scott, *Min. Mag.*, 1914, 17, 143.

² E. S. Larsen, *Amer. Min.*, 1917, 2, 18.

of lead; the material is then ground and levigated. In the cupellation-process, the litharge produced at the beginning is impure, while that last formed contains silver: the middle fractions are collected apart in a conical receiver and, on solidification, this material exfoliates and forms a friable crystalline mass, which is broken up and screened, yielding thereby flake litharge. The harder portions which do not pass the screen are ground with water, the sludge gathered in settling tanks and dried at a low temperature: this is known as levigated litharge. Separation of finely powdered litharge is sometimes effected by air-floatation.

A mechanical furnace for making litharge was patented by Noad in 1895 and was modified and improved later by Barton¹⁾ and others. It consists essentially of an iron pan, fitted with a cover and stirring paddles and connected with fume-condensing chambers by an upright shaft. Molten lead is fed in through a side pipe during the operation. Lead is heated in the pan to a temperature of 600° C., stirred and splashed by the paddles and treated with a blast of steam and air, which enters through a pipe in the cover. The fume of finely divided lead and lead oxide, mixed with the gases, escapes through the uptake and passes to the condensing chambers. The litharge-dust, collected in these, is sometimes levigated to reduce the amount of blue lead in it, sometimes calcined at a high temperature and then sifted. Attempts have been made, by heating the uptake from the pan, to oxidise the blue lead in the effluent fume so thoroughly that subsequent treatment is not required.

The litharge obtained by this method (new process litharge) may contain 4—7 p.c. of lead: after furnacing, it is canary-yellow in colour and very fine in grain and may then contain as little as 0.05 p.c. insoluble in acetic acid and 0.005 p.c. insoluble in nitric acid, and is thus practically free from grit, metallic lead and lead peroxide. It is especially valuable for proofing fabrics and for conversion into pigments.

¹⁾ Eng. Pat., 1902, 4660.

Typical analyses of commercial samples of lead monoxide are:¹⁾

| | Lead | Copper | Bismuth | Anti- mony | Iron | Insoluble in Acetic Acid. |
|----------------|------|----------|---------|---------------|-------|---------------------------------|
| Process Oxide. | — | 0.000070 | 0.0081 | 0.0066 | 0.019 | 0.079 |
| Fused Litharge | 0.4 | 0.0064 | 0.0005 | 0.0015 | 0.007 | 0.05 |

Lead oxide is slightly soluble in water, the solution being alkaline and capable of absorbing carbon dioxide from the air; it dissolves also in alkali solutions, one part by weight being taken up by 13 of caustic soda, 11 of caustic potash and 9 of lime water. The solution in lime water is used as a hair-dye, the lime softening the hair and the lead darkening it, owing to its conversion into sulphide. It combines with the polyhydric alcohols and saponifies fats, liberating glycerine and being converted into the lead salts of the higher fatty acid; these are employed in lead plasters.

The sp.gr. of the compound is about 9.3; the melting point has been variously determined as 776°, 879°, 888° and 906° (the finely divided compound frits at 700°); it is reduced by carbon monoxide at 100° and by hydrogen at 310°. It acts as a powerful oxidising agent, converting, for example, copper, antimony and zinc into oxides, when fused with these metals; use is made of this property, and of its ability to flux many infusible oxides, in the cupellation of silver-lead and the refining of silver. In the laboratory, it is frequently employed as an oxidising agent in organic chemistry. When molten, it absorbs oxygen, which it gives up on slow cooling; this is probably the cause of its 'falling' or exfoliating on solidification, in virtue of which the large masses prepared in the cupellation-method are easily broken up. With linseed oil, it sets to a hard mass, and a mixture of 1 part of litharge and 8—10 of brick-dust, made into a paste with this oil, is known under the name of Dhil Mastic and used for repairing

¹ C. A. Klein, *Journ. Oil Colour Chem. Ass.*, 1919, Vol. 11, No. 8.

stone facings. It is strongly basic, forming fusible silicates, and this property finds application in glazing earthenware. To obviate the risk of poisoning by the direct use of the oxide, lead frits are prepared by fusing litharge with orthoclase felspar. Another aspect of its basicity is seen in its action on ammonium chloride, with which it forms ammonia and a basic chloride of lead, according to the reversible equation:



The pressure of the ammonia in this system is a function of the temperature: it equals one atmosphere at 42° .¹⁾

The dissociation-pressure of lead monoxide is very low, the temperature corresponding to 0.21 atmosphere, calculated by three different methods, being 2327° , 2587° , 1965° .²⁾ In very high vacua, however, it is decomposed, yielding a mirror of metallic lead, even at 750° .³⁾

Lead monoxide is variously coloured, yellow (canary-yellow, yellowish-green), buff (reddish-brown) and red. The yellow rhombic form results from the heating of the higher oxides, or by heating the red to 720° , or the buff to 620° ; the red tetragonal form is produced by the action of hot 50 p.c. alkali on the yellow or buff; and the buff form is obtained by grinding the red or yellow forms. It has been assumed that the compound exists in two enantiotropic forms, red and yellow, with a transition-point about 587° (Jaeger) or 620° (Ditte, Ruer), but this explanation has been questioned by Glasstone, who finds that the change-temperatures differ widely for the various modifications, and that there is no break in the curve of cooling corresponding to the changes. The phenomena are to be ascribed to difference in the size of the particles which make up the various forms, the yellow, for example being an agglomeration of buff particles; conversion of yellow and buff varieties to red is the result of solution. The difference in solubility in normal caustic soda,

¹ Isambert, *Compt. rend.*, 1886, **102**, 1313.

² S. Glasstone, *Journ. Chem. Soc.*, 1921, **120**, 1914.

³ F. Damm and F. Krafft, *Ber.*, 1907, **40**, 4775.

namely, 0.039 gm.mols. per litre for the buff and yellow, 0.035 gm.mols. for the red, is such as may be explained by difference in the size of the particles. The densities of the varieties depend on their past history, that of the red being 9.28, of the buff 9.23 to 9.33 and of the yellow, 9.20 to 9.53.¹⁾

Hydrates of lead monoxide. The precipitate produced by the addition of an alkali to a solution of lead salt is usually regarded as the hydroxide, $\text{Pb}(\text{OH})_2$, but this has never been prepared in a pure condition. The solution of lead monoxide in water behaves as though it contained this compound, which functions as a feeble monobasic acid, plumbous acid, having, according to Glasstone, the ionization-constant 1.32×10^{-12} at 25°. Definite salts of this acid are unknown.

Two other hydrates have been described, $2\text{PbO} \cdot \text{H}_2\text{O}$ and $3\text{PbO} \cdot \text{H}_2\text{O}$. The first is prepared by the action of air and water on the metal, by precipitating lead acetate with a slight excess of alkali, or in the form of hexagonal crystals by exposing a cold solution of lead monoxide in caustic potash to the air.²⁾ The other hydrate crystallises in octahedra and is formed by precipitating basic lead acetate solution with ammonia.³⁾ Glasstone⁴⁾ has been unable to confirm these formulae, his analytical figures being between those calculated for the two hydrates. The composition corresponds rather to the formulae $5\text{PbO} \cdot 2\text{H}_2\text{O}$ or $8\text{PbO} \cdot 3\text{H}_2\text{O}$ and depends somewhat on temperature and concentration of the reacting solutions, the amount of water present being greater, the higher the temperature and the more concentrated the solutions. It is possible that part at least of the variation in composition is due to adsorption of more or less water and to the formation of solid solutions of two hydrates of the

1 S. Glasstone, *Journ. Chem. Soc.*, 1921, **120**, 1689, 1914, This question has recently been investigated afresh by M. P. Appleby and R. D. Reid (*Journ. Chem. Soc.* 1922, **122**, 2129), who have come to the conclusion that the yellow and red forms of lead monoxide are polymorphic varieties.

2 Lüdeking, *Amer. Chem. Journ.*, 1891, **30**, 120

3 Payen, *Ann. Chim. Phys.*, 1866 [iv], **8**, 302.

4 *Journ. Chem. Soc.*, 1922, **121**, 58.

simpler formulae, $2\text{PbO}\cdot\text{H}_2\text{O}$, $3\text{PbO}\cdot\text{H}_2\text{O}$. These may then be regarded as plumbites, the former the neutral salt $\text{Pb}(\text{HPbO}_2)_2$, the latter the basic salt $\text{Pb}(\text{OH})(\text{HPbO}_2)$.

Triplumbic Tetroxide, Pb_3O_4 , also known als Red Lead or Minium (in the past as Paris Red, Saturn Cinnabar, etc.) finds extensive use in the arts as a pigment, in the manufacture of secondary batteries, and of flint and optical glass; in the last-mentioned operation, it is to be preferred to litharge, because of its oxidising character. The commercial preparation is seldom or never a pure compound, but contains varying amounts of litharge, as well as minute quantities of metals, present in the original materials, or derived in the process of working from the furnace and tools.

It is made chiefly from lead and in two stages; in the first the lead is drossed or converted into massicot at a low temperature (about 340°); in the second the monoxide is tinted or coloured by oxidising it in air at a somewhat higher temperature, which is necessarily short of that at which the dissociation pressure of red lead equals the partial pressure of oxygen in air, that is, about 539° . These two operations may be performed in the same furnace, or in different furnaces.

The drossing oven is a small low-arched reverberatory, with a fire place running along each side, the length from back to front being about 11 feet and the width between the fire-bridges about 8 feet. The bed slopes slightly from back to front and towards a median line. In the front of the furnace are two large, hinged working-doors of cast iron, by which the greater part of the air for oxidation is admitted; the products of combustion, after traversing the chamber, escape in front and are drawn off through a hood, which serves the additional purpose of carrying off dust arising from the operations of charging and discharging the furnace. For convenience in working the charge, the rabble rests on an iron hook, suspended from a chain in front of the furnace. The colouring oven is quite similar, but the bottom is flat and the slope from back to front is not so great. The fuel generally employed is coal; some modern ovens are gas-fired

and have mechanical stirrers, and some are built on the muffle principle, by which contact between charge and furnace-gases is obviated.

The charge for the drossing oven is 20—30 cwts. of pig lead. This is melted down and retained in place by building a dam in front, made of lumps of oxide and fragments of lead obtained by the levigation of a previous charge. As oxidation proceeds, the dross is pushed towards the back of the furnace, and the lead in the pool is agitated and splashed with the rabble, so as to increase the reacting surface. Some lead is always tapped at the end of the process, for the rate of oxidation decreases considerably with progressive purification of the metal. To facilitate drossing, a little antimonal lead is usually added to the charge. The old practice in Derbyshire was to use 1 cwt. of slag lead to 18 cwts. of ore lead.

After the tapping of the unoxidised lead, the charge is raked into iron wagons, cooled and ground between mill-stones with water. The coarser part is used in damming the lead in the drossing oven; the finer, after settling out in tanks, is drained, transferred to the colouring oven and heated at a carefully regulated temperature, until a sample, withdrawn and cooled, shows the required tint. The red lead is then withdrawn, sieved and levigated.

In the manufacture of white lead by the stack process, a certain amount of the white lead (not more than 2 p.c. in a well-conducted operation) becomes stained. This 'off-colour' material is also used in making red lead and is worked either alone or mixed with ordinary materials.

The method of manufacturing red lead, proposed by Liebig and Wöhler, namely by fusing 4 parts of litharge with 1 part of potassium chlorate and 8 parts of potassium nitrate, is no longer used, but a limited amount is made by oxidation of lead (or litharge) with sodium nitrate. The nitrate is melted in iron pans, heated to 340°, and the calculated amount of lead in thin strips added. When the oxidation of the metal is complete, the mass is poured into warm water and the sodium nitrite recovered from the liquors, after these have

been neutralised with sulphuric acid, by evaporation. The sodium nitrite is used in the dye industry, for the purpose of diazotisation. In a similar manner, litharge can be prepared from lead and sodium nitrate; the product is, however, impure and the method is rather one for preparing sodium nitrite than litharge.¹⁾

Orange lead, or orange mineral, is a variety of red lead produced by the calcination of white lead. Formerly, the froth from the white lead washing tanks was used for this purpose. The furnace-product is purified either by grinding finely and sifting, or it is water-ground, dried, and sifted. This variety is used for the production of paints, colours, printing inks, and enamels. The finest grades have a vivid orange tint. Orange lead differs from red lead, not only in colour, but also in bulkiness, size of grain, and in its behaviour towards linseed oil. It is much more bulky than red lead; the measures of equal weights of the two being as 7:5. This property is of great importance in the printing-ink trade. When orange lead is mixed with linseed oil or varnish, the mixture remains soft on keeping, whereas red lead soon sets up with these media and the product cannot be thinned again. It is customary, therefore, when using red lead as a paint, to mix it shortly before use.

Commercial varieties of red lead vary considerably in their content of active (peroxidic) oxygen. The peroxide equivalent of this in the pure compound, Pb_3O_4 (*i.e.* proximately $2PbO.PbO_2$), is 34.9 p.c. A good average brand may contain 23—25 p.c.; extremes contain 5 and 34 p.c.

Those with the highest amount of active oxygen are used as pigments, since the poorer grades, with about 12 p.c. of monoxide or more, set up quickly with linseed oil. It is stated, however, that samples with a few per cents. of monoxide are preferable as pigments to those, the composition of which agrees with the formula Pb_3O_4 . When used for making accumulators, the content of peroxide is usually specified; for

G. T. Morgan, *Journ. Soc. Chem. Ind.*, 1908, 27, 483.

use in the match industry, it should be 28—32 p.c. For similar conditions in the colouring furnace, each kind of monoxide shows a maximum peroxidation, more or less definite, though the time required to establish this varies considerably. The past history of the monoxide affects the progress of oxidation. Thus both yellow and red litharge are roasted to red lead much more slowly after washing with water, than after air-separation.¹⁾

The composition of a good commercial red lead is: $\text{PbO}_2 = 26.5$; Insoluble in nitric acid $= 0.075$. $\text{Ag} = 0.0008$; $\text{CuO} = 0.006$; $\text{Sb}_2\text{O}_4 = 0.0004$; $\text{Fe}_2\text{O}_3 = 0.009$; $\text{Al}_2\text{O}_3 = 0.032$ p.c.; cadmium, arsenic, zinc absent.²⁾ Iron, copper, antimony, metallic lead and lead sulphate must be absent when the red lead is to be used in the glass industry, and iron should not exceed 0.005 p.c. when it is used for accumulator plates.

The effect of various factors on the rate of oxidation of litharge to red lead has been studied by J. Milbauer.³⁾ It depends more on the source of the litharge than on the size of the particles, and is decreased by the addition of small quantities of nitric acid and ammonia, but increased by the nitrates of lead and sodium. Of the metals, silver facilitates oxidation at 300° , but its influence is not observable at a higher temperature; bismuth is inert and zinc and antimony act unfavourably. The velocity of oxidation also depends on the temperature and on the partial pressure of the oxygen.

Brown and Nees (*op. jam cit.*) state that the yellow and unfused varieties of litharge are more slowly oxidised than the red and fused forms. They have determined, under laboratory conditions, the optimum temperature of oxidation of various materials to red lead. This is 425° — 430° for white lead, and 450° — 470° for litharge and lead sponge (the latter obtained by electrolysis both acid and alkaline solutions of lead).

1 O. W. Brown and A. R. Nees, *Journ. Ind. Eng. Chem.*, 1916, **4**, 867.

2 C. A. Klein, *op. cit.*

3 *Chem. Zeit.*, 1909, **33**, 552, 950; 1910, **34**, 139, 1341; 1915, **39**, 858.

According to their experiments, lead is not directly oxidised to red lead, but only *via* the monoxide.

These observers have also studied the microscopic structure of red lead and have determined the density of numerous specimens. The following is a brief abstract of the results. Red lead may be either crystalline or amorphous; no definite form can be made out for the crystalline varieties. The specific gravity varies from 8.32 to 9.16; it is lower, the more nearly the composition approaches to Pb_3O_4 , and its value depends on numerous factors, such as the temperature of oxidation, the length of time of heating, and the physical character of the original material. The apparent density depends mainly on the fineness of the particles, decreasing as the fineness increases up to a certain point.

The cause of the variation in colour of the many grades of red and orange lead is not known. It has been found, in laboratory experiments, that small quantities (0.1 p.c.) of lead nitrate and caustic soda have a considerable effect, producing, in the first case, a pink colour, and, in the second, an intense red. When red lead is made by heating monoxide and peroxide of lead with caustic potash, the depth of colour depends on the concentration of the alkali. These facts, however, throw no light on the variations observed in large-scale operations. In these, the nature of the original materials, the furnacing temperature, and other factors, have a determining effect on the colour of the product. Of the impurities, bismuth has the greatest effect on the colour.

Red lead assumes a darker shade of red on heating, becoming violet and ultimately black; it regains its original tint on cooling. At a higher temperature, it evolves oxygen and leaves a residue of yellow monoxide; this reaction is rapid and complete *in vacuo* at 530° . Heated in a closed space, between certain limits of temperature, the compound is dissociated into litharge (greenish-yellow in colour) and oxygen, and an equilibrium-system of two components in three phases is established. The dissociation-pressure of the compound is thus a function of the temperature. The pressure-temperature

curve has been determined by Reinders and Hamburger¹⁾ between the temperatures 445° and 607°. It is smooth and gives no evidence of the formation of intermediate compounds, or solid solutions. Some of the values are:

| | | | | |
|---|------|------|------|------|
| Temperature . . . | 445° | 500° | 555° | 636° |
| Dissociation-pressure (mm mercury) . . | 0.5 | 60 | 183 | 763 |

The dissociation-pressure is 0.21 atmosphere at 539° C. The values calculated by Glasstone, by different methods are 573° and 570°. When the oxide has been purified by extraction with solutions of acetate or nitrate of lead, equilibrium is much more slowly attained than when the oxide is crude.

Red lead is extremely insoluble in water, the solubility-coefficient being 5.32×10^{-51} .²⁾ It is soluble in glacial acetic acid, slowly converted into lead peroxide and lead acetate by dilute acetic acid; nitric acid liberates the peroxide and lead nitrate passes into solution. Cold oxalic acid does not reduce red lead, but this is effected by digestion with nitric acid and a little sugar or alcohol.

Pure triplumbic tetroxide was prepared by Dumas³⁾ by oxidising litharge with oxygen and by extracting the orange variety (*mine orange*) with solutions of lead acetate and caustic potash. The products contained 9.34 p.c. of oxygen and lost 2.34 p.c. on heating. Levol⁴⁾ prepared it by fusing 100 parts by weight of litharge, in a platinum or silver crucible, with 25 of potassium chlorate and 200 of potassium nitrate, the temperature being maintained at a dull red. The residue was extracted with potash solution and washed. Another method of his was to boil alkaline plumbite solution 1—2 hours with lead peroxide, removing the slight amount of peroxide by digesting the product with cold oxalic solution and then the oxalate with caustic potash. Similar methods which have been

1 *Zeitsch. anorg. Chem.* 1914, **89**, 71.

2 S. Glasstone, *Journ. Chem. Soc.*, 1922, **122**, 1456.

3 *Ann. Chim. Phys.*, 1832, **49**, 398.

4 *Ibid.*, 1840, **75**, 108.

employed are¹): heating lead peroxide with nitre at 470° and extracting the product with water; and heating a mixture of 3 equivalents of lead monoxide and 2 of lead peroxide with a solution of potash, containing 200 grams of the solid alkali dissolved in 100 c.c. of water.

Dumas regarded red lead as plumbous plumbate—"un oxide salin un plomate de plomb, dont lequel la base renferme la même quantité d'oxygène que l'acide, sa formule étant $2\text{PbO}, \text{PbO}_2$ ". This view has been generally accepted and has received confirmation from the electrochemical study of the compound, from which it appears to function as a plumbous salt.²) Its formation by the oxidation of litharge is thus to be viewed as the result of the combination of the basic monoxide, with the acidic dioxide, which is its initial oxidation-product. Under particular conditions of oxidation, the meta- or the pyroplumbate may be formed in a similar manner (*v. infra*).

If a mixture of litharge and red lead of high active oxygen-content be compared with a red lead of lower active oxygen-content, but equal to that of the mixture, it will be observed that they differ, especially with respect to their behaviour towards linseed oil. Such facts have led to speculations on the chemical nature of red lead and its relationship to litharge. Mendeléeff's hypothesis of the polymerisation of lead monoxide (and other oxides) has been applied by Wade to the problem under consideration. It is assumed that the polymeride has some such formula as $\text{Pb}_{12}\text{O}_{12}$; that oxidation of litharge takes place gradually and uniformly through the mass and in such a way that successive stages, $\text{Pb}_{12}\text{O}_{13}$, $\text{Pb}_{12}\text{O}_{14}$, &c., are passed through. When the stage of oxidation represented by $\text{Pb}_{12}\text{O}_{16}(=4\text{Pb}_2\text{O}_4)$ is reached, then pure red lead is the product. This view, however, has little to recommend it.

Lead Sesquioxide, Pb_2O_3 , is apparently only known in the hydrated form, $\text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and is a constituent of the yel-

1 Milbauer, *Chem. Zeit.*, 1914, **38**, 477, 559, 566, 587.

2 S. Glasstone, *Journ. Chem. Soc.*, 1922, 1456.

lowish-red precipitate formed on oxidising lead monoxide, dissolved in alkali (that is alkali plumbite) with hypochlorite or hypobromite solutions¹⁾ or by the reaction of alkali plumbite and plumbate.²⁾

The two methods are essentially the same, since the initial stage of the first process is the oxidation of plumbite to plumbate. Purification of the precipitate is effected by utilizing the fact that the solubility of the hydrated sesquioxide in alkali is intermediate between that of lead monoxide and lead dioxide. The method of preparation, elaborated by Glasstone³⁾, is as follows: 250 c.c. of 12 p.c. caustic soda solution is saturated with litharge, diluted to 500 c.c. and the same volume of bromine water added. After standing overnight, the precipitate is washed by decantation with very dilute acetic acid, then stirred with a solution of 60 grams of caustic soda in 300 c.c. of water at 50°. The sesquioxide is precipitated from the filtrate by the addition of acetic acid (40 grams of glacial acid and 150 c.c. of water). Dissolution in alkali and precipitation with acid are repeated if necessary. The purified powder, dried in a dessicator, is brown, and contains equivalent amounts of plumbous and plumbic lead, and the water-content approximates to that required for the formula $\text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

The hydrated compound loses water at 200° and is apparently resolved into a solid solution of monoxide and dioxide of lead, the dissociation-pressure of such a mixture and of the sesquioxide being the same. From the electrochemical behaviour of the compound, Glasstone infers that it is a plumbous salt, and it may thus be regarded as plumbous metaplumbate, $\text{Pb}(\text{PbO}_3)$, or expressed on an analytical basis, $\text{PbO} \cdot \text{PbO}_2$; since the existence of the sesquioxide seems to be conditioned by its water-content, it is perhaps preferable, to represent it as the plumbous salt of hydrated metaplumbic acid, $\text{Pb}[\text{Pb}(\text{OH})_3]$, as suggested by Bellucci and Parravano.⁴⁾

1 Winkelblech, *Annalen*, 1837, **21**, 21.

2 Frémy, *Ann. Chim. Phys.*, 1844 [III], **12**, 448.

3 *Journ. Chem. Soc.*, 1922, **122**, 1456.

4 *Zeit. anorg. Chem.*, 1906, **50**, 107.

The oxide Pb_3O_8 is said to be formed as a dark brown powder by heating monoxide, peroxide or carbonate of lead to $400\text{--}500^\circ$ in oxygen, at a pressure of 100 atmospheres.¹⁾ So far as its composition is concerned, it may be looked upon as plumbous pyroplumbate, $\text{Pb}_2(\text{Pb}_3\text{O}_8)$, the relation of pyro- to ortho-plumbic acid being represented thus:—



Lead Dioxide, PbO_2 , (Lead Peroxide or Puce-coloured Oxide of Lead) is found native as Plattnerite, a black mineral, sp.gr. 9.4, which crystallises in hexagonal prisms. A similar compact, greyish-black oxide, sp.gr. 9.36, hardness 5—6, has been prepared by the electrolysis of lead nitrate solution.²⁾ Other methods of preparation are: by the action of chlorine or nitric acid on red lead; by the oxidation of lead acetate in boiling solution with hypochlorites; by the oxydation of a strongly alkaline plumbite with potassium persulphate³⁾ or diazobenzene perbromide⁴⁾, or of lead oxide with alkaline permanganate or ferricyanide; by oxidising the monoxide in molten caustic soda with sodium nitrate⁵⁾ and by the action of hydrogen peroxide on a solution of lead nitrate in 20 p.c. caustic soda.⁶⁾

It can be prepared directly from lead sulphide, when this is used as anode in the electrolysis of dilute (less than 1 p.c.) acids, alkalis or salts⁷⁾ the lead being converted to oxide, the sulphur to sulphuric acid; lead sulphate may also be used as a source of the peroxide, by mixing it with magnesia and passing chlorine through the mixture, suspended in hot water.⁸⁾ The last method is of practical importance; the

1 F. Fischer and H. Ploetze, *Zeit. anorg. Chem.*, 1912, **75**, 19.

2 W. Palmaer, *Midd. K. Vetenskapsakad.*, Nobel. Inst., 1919, **5**; No. 13, 1.

3 Panoplus, *Chem. Zeit.*, 1916, **40**, 339.

4 Guttman, *Ber.*, 1912, **45**, 829.

5 Minor, *Journ. Soc. Chem. Ind.*, 1894, 940.

6 Zotier, *Bull. Soc. Chem.*, 1917, **21**, 244.

7 Eng. Pat., 1901, 12186.

8 Friedrich, Mallet and Guye, *Monit. Scient.*, 1906, **20**, 514.

magnesium is left in solution as sulphate and chloride and the lead peroxide is purified by boiling with 10 p.c. caustic soda solution and then with hot dilute nitric acid: the yield is almost quantitative. Lead peroxide is sometimes formed by the evaporation of solutions of litharge in turpentine. A hydrated form is produced by the electrolysis of alkaline solution of lead tartrate.¹⁾

When a drop of solution of litharge in potash is electrolysed in a platinum dish, the dish forming the anode and a platinum wire, dipping into the solution, the cathode, a film of lead peroxide is deposited on the dish, thickest under the wire and decreasing in thickness towards the periphery of the drop. This gives rise to coloured rings which are known as Nobili's rings.

It is a dark brown, almost black, powder, sp.gr. 9.35–9.45 for the natural, 8.9–9.19 for the artificial forms and is best kept in the moist state. On exposure to sunlight it changes to red lead, and is dissociated on heating, yielding solid solutions of the mono- and di-oxides: there is no evidence of the formation of red lead, or any other oxide but litharge in the process.²⁾ Its chief use is in the manufacture of accumulator plates, in the dye industry and in making Swedish matches. It has a powerful oxidising action, taking fire when triturated with sulphur, and igniting sulphuretted hydrogen when the latter is passed over it, the heat of this reaction being such that explosives like guncotton or picrate can be fired and metallic powders ignited by its aid.³⁾ A large number of organic compounds, when triturated with it, also cause an evolution of heat and light. Lead peroxide combines readily with sulphur dioxide, forming lead sulphate. It can be used for separating sulphur dioxide from carbon dioxide and is often employed for this purpose, and as an oxidising agent, in the analysis of organic compounds containing sulphur by the Dennstedt process. The statement of Weil⁴⁾, that the peroxide used for

1 Wernicke, *Pogg. Ann.*, 1870, **139**, 132.

2 Reinders and Hamburger, *Zeitsch. anorg. Chem.* 1914, **82**, 71.

3 Vanino and Hauser, *Ber.*, 1900, **33**, 625.

4 H. Weil, *Ber.*, 1910, **43**, 149.

this purpose sometimes contains carbonates, difficult to remove even by digestion with nitric or phosphoric acids has been denied by Dennstedt¹), who ascribes the liberation of carbon dioxide from the peroxide to organic contamination, and proves that neither monoxide nor peroxide is able to absorb carbon dioxide at temperatures from 100° to 350°.

Other examples of the oxidising properties of lead peroxide are seen in its action on warm hydrochloric acid, in which chlorine is evolved; in its conversion of chromic hydroxide, in presence of alkali, to a chromate and of manganous salt, in presence of nitric acid, to a permanganate. It oxidises carbon monoxide at 80°, being itself reduced to litharge and the initial products of reaction unite to form lead carbonate; with nitrogen peroxide, a similar reaction leads to the formation of lead nitrate. It is reduced by hydrogen at 190° to litharge. It decomposes hydrogen peroxide catalytically, but, in presence of nitric acid, lead nitrate passes into solution and oxygen is quantitatively liberated.

Besides being a peroxide, as illustrated in many of the above reactions, lead peroxide is at once a feebly basic and a feebly acidic oxide. Evidence of the former property is the existence of unstable plumbic salts, derived from it, in which the lead is presumably quadrivalent, and of the acidic nature, the existence of plumbates, salts in which the lead exercises the acidic function. These plumbates belong to two types, the orthoplumbates, M'_4PbO_4 and the metaplumbates $M'_2PbO_3 \cdot 3H_2O$ or $M'_2Pb(OH)_6$. Many derivatives of both classes have been prepared²) and, as already observed, there is some justification for regarding red lead and lead sesquioxide as salts, respectively, of ortho- and meta-plumbic acids.

The orthoplumbates evolve oxygen on strongly heating and on this property a method, suggested by Kassner, was based for preparing oxygen from air on a large scale. Litharge and calcium carbonate, mixed together, are heated in a stream

¹ *Ber.* 1910, **43**, 1197.

² Frémy, *Ann. Chim. Phys.*, 1844, [III], **12**, 496; Bellucci & Parravano, *Gazz. chim. ital.*, 1905, **35**, [II], 500.

of air, when oxygen is absorbed, calcium plumbate, Ca_2PbO_4 , is formed as a reddish brown powder and carbon dioxide is evolved. If the plumbate be now heated in a current of carbon dioxide, at a higher temperature, the original materials, litharge and calcium carbonate, are regenerated and oxygen is liberated. This cycle of reactions can then be repeated.

Lead peroxide, warmed with concentrated alkali, passes into solution and, on cooling, deposits crystals of the meta-plumbate, $\text{K}_2\text{PbO}_3 \cdot 3\text{H}_2\text{O}$. When this compound is brought into water at the ordinary temperature, it is completely hydrolysed, and *plumbic acid* H_2PbO_3 remains in solution in the colloidal state.¹⁾

CHAPTER XI

THE CARBONATES OF LEAD—WHITE LEAD

The normal carbonate of lead, PbCO_3 , occurs naturally as the mineral cerussite and is produced by precipitation of cold solutions of nitrate or acetate of lead by means of ammonium carbonate and by the action of carbon dioxide on a solution of lead acetate.²⁾ It is sparingly soluble in water, the saturated solution at 20° containing only 0.0017 gram of lead carbonate per litre. Like the other insoluble carbonates of bivalent metals, it dissolves in carbonic acid, owing to the formation of a soluble bi-carbonate, and the extent to which this takes place depends on the concentration of the carbonic acid. This is brought out in the following table, which shows the solubility of the lead, reckoned as normal carbonate, in solutions of carbonic acid of varying concentration:

| | | | | | | | |
|---|------|-----|-----|------|------|------|-------|
| Carbon Dioxide (mgm per litre) | 0 | 2.8 | 5.4 | 14.4 | 26.0 | 43.5 | 106.0 |
| Lead Carbonate (mgm per litre) | 1.75 | 6.0 | 7.0 | 8.2 | 9.9 | 10.9 | 15.7 |

1 Bellucci and Parravano, *Atti. R. Accad. Lincei* 1906, **15**, [II], 542, 631; Parravano and Calcagni, *Gazz. chim. ital.* 1907, **37**, [II], 2646.

2 Rose, *Pogg. Ann.* 1857, **84**, 66.

As the bicarbonate of lead is readily dissociated into normal carbonate and carbonic acid, it has not been isolated in the free state, but exists only in contact with its dissociation-products.

Basic carbonates of lead are ill-characterised and are the usual products of precipitation of lead salts with carbonate solutions, especially at the boiling temperature. Normal lead carbonate suffers hydrolysis, even at 70°, the liquor acquiring an alkaline reaction; on continued boiling, there is progressive loss of carbon dioxide, until the solid approximates in composition to a basic carbonate of the formula: $3\text{PbO} \cdot 2\text{CO}_2 \cdot \text{H}_2\text{O}$.¹) Evidence of the formation of a definite basic carbonate of the same composition has also been obtained from the study of the solubility-relations of oxide and normal carbonate of lead in 20 p.c. sodium acetate solutions; a definite break occurs where the composition of the solid phase agrees with that of this basic carbonate, and there is no indication of the formation of solid solutions.²)

These observations are of importance, since the presence of this basic carbonate in white lead is almost universally admitted.

WHITE LEAD

One of the earliest of the chemical industries was the manufacture of a white pigment from metallic lead. It has already been pointed out that the methods and materials employed in this work leave little doubt that the preparation, which the ancients knew under the names of *psimythion* and *cerussa* was, in fact, white lead, and it may be surmised that the differences in chemical composition and physical properties between their manufactures and ours did not greatly exceed those which exist between certain samples of white lead on the market at the present day.

The lack of precise chemical and physical criteria, whereby

¹ Salvadori, *Gazz. chim. ital.*, 1904, **34**, [1], 87; C. A. Klein, *Journ. Oil and Colour Chem. Ass.*, 1919, [11], No. 8.

², L. F. Hawley, *Journ. Phys. Chem.*, 1906, **10**, 654.

white lead can be characterised, has been the cause of some misunderstanding in connexion with this subject, and the use of such trade-names as innocuous white lead, non-poisonous white lead, sublimed white lead, for preparations which bear but little chemical resemblance to the typical corrosion-product of lead has naturally added to the confusion. It must be emphasized that white lead is not a compound; it is a preparation of varying composition, and it by no means follows that two specimens, identical in ultimate composition, are chemically the same. A mixture of lead hydroxide and normal lead carbonate, for example, might yield the same analytical results as a basic carbonate of lead, and, on the other hand, two samples, chemically identical, may be very different in their behaviour as pigments.

It has, however, been generally recognised, from time immemorial, that white lead is the product of the corruption or corrosion of lead by means of vinegar, in an environment of decaying organic matter; that is, under such conditions as promote a gentle heat and yield a supply of carbon dioxide. With the progress of discovery and invention, the original methods have been modified, even to the extent of omitting the acetic acid, but without radically affecting the composition and properties of the product. Such products, then, legitimately take the same name. The extent of variation in composition and properties which would justify the abandonment of the name has never been determined, nor would it be profitable to do so, but the admission of pigments, totally different in chemical nature, into the category of white leads, can hardly be justified on historical grounds. They should be known as white lead substitutes, and as such will be described later.

Before proceeding to the detailed description of the methods used in making white lead at present, a brief survey will be made of the more important processes which have been suggested, some of which have not stood the test of time. The production of white lead from the metal involves changes of oxidation, hydration, and carbonation. For a long period, the successful accomplishment of these was only

possible by the intervention of acetic acid, and even to-day, most of the white lead is produced by the agency of this acid, the processes having been developed, to a large extent, on empirical lines.

During the last two centuries, many suggestions have been made and tried for the improvement of the method, either in the direction of shortening the lengthy time of action, of providing more easily controlled sources of heat, acetic and carbonic acids, or of simplification or better regulation of the chemical reactions.¹⁾ The substitution of other fatty acids has been suggested, but little practical advantage is to be expected from the higher homologues, owing to their greater cost, while the first member of the series, formic acid, has been proved by Pelouze²⁾ to be incapable of replacing acetic acid, probably owing to the fact that it does not form a basic lead salt. The substitution of pyroligneous acid for beer-vinegar is an obvious change, and the suggestion of Fishwick, in 1787, to employ "used tanner's bark" in place of dung and stable litter as a source of heat and carbon dioxide has been generally approved.

The Klagenfurth method, used extensively in Carinthia, for the corrosion of the virgin lead of Bleiberg, marks an early stage in the development of the Stack process. Heat was generated in a lower room and rose through a loose floor into the corroding room above, in which were packed wooden boxes, containing lead, acetic acid and materials like wine lees, grape skins, etc. which, by their fermentation, yielded the necessary carbon dioxide. One may see in this process a fore-shadowing of the Chamber process, in which the heat and the reacting gases are all generated externally to the corrosion-chamber itself, which, at the beginning of operations, contains only the lead (and air).

Two characteristics of the all-important Stack and

¹ For an account of the patents taken out since the earliest, that of Eland, 1622, for 'makinge white and redde leade', until recent times, see *Chem. Trades Journ.*, 1890, 7, 159, 210, 272, 318.

² *Ann. Chim. Phys.*, 1842, 3rd. Ser., 4, 104.

Chamber processes are the somewhat massive condition of the lead and the simultaneous action of the two acids concerned in its corrosion, namely, acetic and carbonic acid. Some of the attempted improvements have, for their object, the speeding up of the velocity of reaction by the comminution of the metal, and the separation of the action of the acids in point of time.

The process of Bailey is an example of the first. The lead was used in a fibrous state, packed in boxes, and was exposed to the conjoint action of acetic acid, carbon dioxide, steam and air; in this way, the time of corrosion was shortened to three days. This method was tried in the United States but did not prove successful.

Carter's process, which has been used in the United States and Canada, combines comminution of the metal with separation of the reacting acids. Coarse, granular, blown lead is brought into large revolving, wood-drums and sprayed first with acetic acid and water, and then carbonated. This treatment is repeated frequently, the whole process lasting twelve days. The method thus provides for constant renewal of a large surface of metal, for its conversion into basic acetate and the precipitation of white lead from this in several successive reactions. It is said to have been worked successfully.

Complete separation of the two acids, which are used in so many of the white lead processes, is attained by carbonation of the ready-prepared basic acetate of lead. This may be made initially from lead-splashes, or from litharge. In either case, the ratio of oxide to acetate in the material submitted to carbonation may be very high (of the order 100:1), since there is constant regeneration of acetic acid, though free only momentarily, and this, as it were, permeates the whole mass of litharge during the progress of reaction.

Thénard's process, and its modifications, illustrate this type. It was invented in 1801 and put into operation by Roard and Brechot at Clichy, which name, as well as that of the French process, it often bears. Litharge was dissolved in pyroligneous

acid to form the basic salt, and into the solution of this, of definite concentration, carbon dioxide, generated in kilns, was blown for 10—12 hours, until the liquor was neutral, or showed faint acidity. After separation of the precipitated white lead, the liquor, now containing normal lead acetate, was used to dissolve a fresh quantity of litharge. This process was introduced into England by Gossage and Benson, but given up about 1880, apparently owing to the difficulty of preventing the precipitation of an undue amount of normal lead carbonate. It has been revived, in recent years, by Sharpe, who causes carbon dioxide to be blown under pressure through a series of boxes, containing the material prepared by mixing water, litharge and acetic acid in the proportions by weight 1600:400:1.

The Matheson process is a successful modification, by Dahl, of this method and is used in the United States. The lead is feathered by running it in the molten condition into water, then put into tubs with acetic acid and blown with air and live steam. This is followed by carbonation, the gas being generated in coke furnaces; the lead is completely corroded in this process.

Though by no means exhausting the modifications of the classic method, these examples serve to show some of the variations which are possible, or have been thought so, in practice. Radically different methods, in which acetic acid is dispensed with altogether, have also been proposed, and some of them carried to a successful issue. The direct carbonation of lead monoxide is a difficult matter, as pointed out long ago by Pelouze, though, as we have seen, it can be simultaneously carbonated and hydrated in presence of solution of lead acetate; and, as MacIvor has shown on a large scale, in presence of ammonium acetate also. The hydration of lead monoxide, too, is not readily accomplished. On the other hand, the sub-oxide of lead lends itself with ease to oxidation, hydration and carbonation, and this property is utilised in the mild process of Rowley, in which the sub-oxide is made from lead, and in the Bischof or Brimsdown process, in which litharge is the raw material; details of these methods,

of great interest from the chemical point of view, will be given later.

Electrolytic methods have been suggested for the preparation of white lead. In one of these, the anode is of soft lead, the cathode of hard lead, and the electrolyte consists of a 1.5 p.c. solution of sodium chlorate and sodium carbonate, containing these salts in the proportion of 4:1. Carbon dioxide is passed through the electrolyte and this effects the carbonation of lead hydroxide, immediately this is formed at the anode. Another suggestion is to bubble air and carbon dioxide through sodium carbonate solution, in which colloidal lead is dispersed by the cathode discharge. This is stated to yield white lead of good quality, but the consumption of energy is high.¹⁾

One feature common to most of the processes described above is that either lead bases (various hydrated oxides), or the basic acetate of lead is presented to the action of carbon dioxide. Only in this way can the basic carbonate (or carbonates) of lead, which bulks largely in good preparations of white lead, be obtained. It is, however, difficult in such processes to prevent the formation of normal carbonate or sandy lead, and it is partly at least with this object in view that other basic salts have been utilised.

Button and Dyer proposed carbonation of the hot solution of the crystalline basic nitrate, $2\text{PbO} \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$, a salt readily made by dissolving litharge in solution of normal lead nitrate, and so reactive towards carbon dioxide that it absorbs the gas quickly from air. Brouner prepares a basic sulphate $3\text{PbO} \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$ by the action of caustic soda on precipitated lead sulphate at 70° , and converts this into white lead by precipitation with sodium carbonate. Hof carbonates the mixture of basic chlorides of lead and magnesium, produced by dissolving litharge in magnesium chloride. Milner bases his suggestion for the use of basic chloride of lead on Scheele's observation, that litharge and common salt react to form

¹ G. Bredig and F. Haber, *Ber.*, 1898, **31**, 2741.

caustic soda and the basic chloride of lead. If carbon dioxide be passed into the mixture until its reaction is neutral, sodium carbonate is formed, which reacts with the basic chloride to yield white lead. These suggestions are of interest as showing the important part which basic salts play in the production of white lead, but it would appear that they are without practical significance.

About two-thirds of the world's production of white lead is made by the Stack or Old Dutch process, the lineal descendant of the method described by the classical writers. The total yearly production of white lead is estimated at 275,000 tons, of which 180,000 tons are made by the Stack process, 45,000 tons by the Chamber process, and 50,000 tons by other methods.¹⁾ About one quarter of the pig lead produced is converted into white lead.

THE STACK PROCESS

The history of the early stages of development of this process has already been detailed. Coming to more recent times, there is a short, but singularly comprehensive, description by Vernatti²⁾ of the Venetian method, as practised 250 years ago, which deserves to be read even at the present day. The author describes the casting of soft lead into plates. "These are rolled with some art, round; but so as the surfaces nowhere meet to touch: for where they do no ceruss grows". The rolls are placed in pots, just capable of holding one, but so as not to touch the vinegar, and covered with a plate of lead. Horse dung is the bedding material and each heap consists of 4 beds of 400 pots each, or 1600 in all. After 3 weeks, the heap is taken down, the strips unrolled and beaten with battledores and the white lead ground, washed, moulded and dried in the sun.

"The accidents to the work are: That two pots alike ordered, and set one by the other, without any possible distinction of advantage, shall yield the one thick and good

¹ C. A. Klein, *Oil and Colour Trades Journal*, Dec. 6, 13, 1913.

² Sir Philiberto Vernatti, *Phil. Trans.*, 1678, **12**, 935.

plates, the other few and small or none: which happeneth in greater quantities, even over whole beds sometimes. Sometimes the pots are taken up all dry, and so sometimes prove best; sometimes again they are taken up wet . . . the plates which cover the pots yield better and thicker plates than do the rolls in them. And the outsides, next to the planks, bigger and better than the insides, next to the rolls, and the spirits that first arise out of the vinegar. We therefore question much, whether the strongest bodied vinegar, or the quickest and sharpest, be the most effective."

About a century later, the English and the Dutch had the monopoly of the manufacture of white lead and the methods, as practised at Rotterdam, Amsterdam and Sheffield, were examined and described by Jars.¹⁾ The stacks held up to 15,000 pots, each stack having 4 compartments which contained 5 beds or sets of 750 pots. Beer-vinegar was used in the pots and dung formed the source of heat and carbon dioxide. The time of reaction was 4—5 weeks in Holland and 6—8 in England. The harder scale from the plates overlying the pots was ground separately and sold as *Blanc du Plomb*, the softer material from the rolls was ground with chalk and sold as *Ceruse*, at a lower price. The pulp from the grinding mills was filled into unglazed, conical pots, dried in sheds, protected from sun and rain, and the moulds turned out after 5—6 weeks and the drying completed under natural conditions, 4 months in all being required in summer and 6 months in winter.

In the process as carried out at present, great importance is attached to the purity of the metal and corrodors generally submit it to a special refining before corrosion. Returns from the stack are remelted. Even small amounts of foreign metal retard the action; 0.02 p.c. of bismuth renders the lead 'common' and gives a grey tint to the product; it also makes the cores spongy and granular, with the result that the metal accumulates in the millstone grooves; a minute quantity of

¹ *Voyage Métallurgique*, Tome II. pp. 530—570. Paris, 1780.

silver causes the formation of a pink colour; copper, too, even in small quantity is objectionable, and antimony retards corrosion if above 0.05 p.c. and 0.1 p.c. of the metal spoils the colour of the white lead. A typical corroding lead contains:¹)

Ag=0.0006, Bi=0.01, As=0.005, Sn=0.0003,

Fe=0.0015, Total 0.0174 p.c.

The substitution of spent tan for stable litter minimises the risk of discoloration of the white lead by sulphuretted hydrogen, but the fermentation is somewhat slower, and consequently the conversion of the 'blue' lead into white lead requires a greater length of time. The fermentation of the tan is thought to be due, at first, to bacterial action. In any case, heat is developed and the temperature may rise to 80° C., though 50°—60° is more usual. The carbon dioxide necessary for the process is produced in the fermentation, and the tan parts with much of its water. Some old tan is used in the building of a new stack and the behaviour of the tan mixture is closely observed at the beginning of operations, as it is of the greatest importance that it should be in the right condition.

The lead is cast into thin sheets of lattice work or gratings, so as to expose a large surface to reaction, and ribbed on one side, so that on stacking there is always an air-space between, by pouring molten lead on to a sloping grooved iron plate, from which, on solidifying, the crates, buckles, plates, straps, or wickets, as they are variously styled, are easily detached. Some is also cast in thin circular discs or stars. In some works the casting is done on a machine, consisting of an endless band of square plates of iron linked together, each plate being a mould, into which the lead is poured as the plates are slowly moved under the spout of the lead-pot. The castings are delivered at the end on to a leather belt, covered with plates of sheet iron to prevent the hot lead injuring the leather. This machine can make from 50—60 castings per minute.

The corroding house or stack is a brickwork chamber, having an area from 12 feet by 20 feet, to 20 by 40 feet, and

¹) C. D. Holley, *The Lead and Zinc Pigments*, 1909.

a height of 25 feet. These are usually built in batteries, two neighbouring chambers having a wall in common. The front wall of the chamber is provided with an opening, 4 feet wide, running from the top to the bottom, which serves for the introduction of the materials used in the construction of the stack. As the building of the stack proceeds, the opening is closed by boards, fitting into slots, the top being, however, left open for the purpose of inspection. The stack is built up as follows: First, the floor of the chamber is covered with a layer of ashes, upon which is spread spent tan, already in a state of fermentation; the thickness of this first bed of tan is 3 feet. The tan is beaten down and the surface levelled, and on the bed so formed earthenware pots, partially filled with a 2 or 3 p.c. solution of acetic acid, are placed side by side, leaving a space about 9—12 inches wide between the outside rows and the walls of the chamber. The pots ordinarily used are of two sizes; the larger ones are provided with a rim on the inside, on which discs of the metal rest. They are placed along the edges and support the wooden bearers, which carry the flooring boards used to cover the set.

The smaller pots, which cover the area partitioned off by the larger ones, contain only the dilute acid. Sometimes, pots of one size only are used, and the flooring boards are supported by blocks of wood. On the top of the earthenware pots are placed the crates of metallic lead, so as to form a layer of lead from 5 to 9 inches in depth; between the lead and the cover of flooring boards is left a space of from 6 to 8 inches. The space between the walls of the chamber and the pots is filled in with tan on all sides, the opening in front being closed by boards. On the bed so constructed, another bed is built in exactly the same way, with the exception that in the construction of the upper beds, the layer of tan is only about 1 foot in thickness. In this way the stacks are filled up to a height of 20 feet or more, and the topmost bed is covered with a layer of tan. Ventilation is sometimes specially provided for, but when excessive it appears to have a harmful effect on the corrosion process.

The arrangement of a stack is shown diagrammatically in Fig. 37.

After the stack is built, it is left to itself for about three months. It is then unloaded, the top covering of tan is removed, and the bark, which is not mouldy, is used to add to fresh tan in the construction of another stack. The corrosions preserve the form of the castings of the metal, but are more bulky, and present a white opaque appearance. They vary in texture; the best corrosions are hard and porcellanous, and can be easily handled without crumbling, whilst the poorer are of a

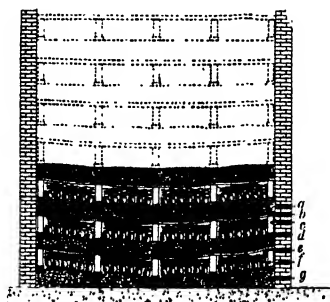


Fig. 37.—The Stack Process (diagrammatic).

a, Floor boards; *b*, Floor beams; *c*, Wood blocks keeping heights apart; *d*, Beams under wood blocks; *e*, Corroding strips of lead; *f*, Earthenware pots containing dilute acetic acid; *g*, Spent oak bark.

floury character and crumble easily when touched. In places the white lead is discoloured, owing to droppings of water containing colouring matter derived from the tan. Before removal of the corrosions from the stack, each layer, as it is exposed, is thoroughly moistened with water to keep down the dust. It is usual to find the earthenware pots quite empty and dry, though a few may contain liquid; the pots are washed and drained, and used again. The pieces of white lead which fall on the bed of tan are picked up by hand, the surface of the bed is also raked and a further quantity of white lead is got from the tan by washing it on sieves in a stream of water.

The trays of corrosions taken from the stack are sunk in a cistern of water and the contents are directed, by means of

rakes, between corrugated rollers, running under a stream of water. After the blue lead has been separated, the white lead is crushed by passing through a pair of smooth rollers, made of gun-metal, and raked about over a perforated plate under a constant spray of water. Dollies or centrifugals are also used for the purpose of detaching the white from the blue lead. The churned-up material is shot over a grid, which retains the larger fragments of blue lead. Blue lead which has passed through the grids is separated in special dollies during the grinding operation and the finished white lead contains only a trace of blue lead. The coarse white lead next passes to horizontal grinding stones, to which it is fed by a ladle or by an endless band. After passing through these stones, the white lead issues in the form of a thick white mud, and is again passed through other grinding stones, until it has been reduced to a state of subdivision so fine, that it is carried along by the stream of water to the settling tanks; the white lead which settles out in the troughs used to convey the water to the tanks is returned to the grinding stones. The grinding and levigating are conducted in such a way that the water may be used over again. Sodium carbonate is added during the grinding process to precipitate lead present as soluble acetate and the resulting sodium acetate eliminated in the settling tubs and filter presses. It is essential that white lead should be free from lead acetate.

In the tanks, the white lead gradually settles and forms a thick white sludge or slurry, from which the water is syphoned off, and when the mud has attained a sufficient consistence, it is ladled out into the dishes used for drying it. The dishes are shallow clay saucers, 12 inches diameter and 3 inches deep, and made of clay similar to that employed in making flower pots. The dishes are stacked in drying stoves, upon shelves made of iron bars, the stoves are heated by iron pipes made to circulate round the floor of the stove, and connected with a fireplace outside the stove, the products of combustion from the fire passing through the pipes. In this way the pulp, which contains 25—30 p.c. of water, is gradually dried; the temper-

ature of the stoves should not rise above 180°F. (62°C.). Drying is also carried out in steam-heated copper pans, and under reduced pressure. The white lead when dry is packed in casks, or ground and mixed with oil to form a paint. Refined linseed oil is used for this purpose, and the 'paste' produced contains usually 7—9 p.c. of oil. Softer pastes are sometimes made, containing up to 12 p.c. of oil. During the grinding, some manufacturers add a small quantity of a blue colouring matter, such as Ultramarine Blue to the white lead, in order to correct the somewhat yellowish tint due to the linseed oil.

To obviate the dangers attending the drying of the pulp, the method patented by Ismay¹⁾, and known as wet-pugging, has been adopted with considerable success. In this process, the white lead pulp from the filter presses is mixed with oil and thoroughly agitated in a pug-mill, with the result that the greater portion of the water is displaced by the oil; the last portion of water is driven off by using a pug-mill, provided with a heating jacket, in which the mixture is heated to a definite and regulated temperature in a partial vacuum. This method constitutes a considerable hygienic advance.

In stacks of area 12 feet by 20 feet, 3 tons of lead are set per height and about 1000 pots of $5\frac{1}{2}$ inches diameter, containing 200 gallons of dilute acetic acid. In stacks 28 feet by 14 feet, each height or set may contain as much as 7 tons of lead, the total for a stack of 12 heights being 84 tons.

Corrosion takes place to the extent of 40—80 p.c. of lead, depending, under normal working conditions, on the thickness of the lead straps or buckles, the weight of lead set in a stack and the duration of the period of corrosion. The amount of acetic acid consumed in the process is 40—50 lbs. (absolute) per ton of white lead produced. The acid is evaporated in the top height after about 3 weeks, and from the whole stack in 8 weeks; only 0.08 p.c. is left, as acetate, with the white lead. A great deal of water passes away in the process. A stack with the capacity of 12,000 cubic

Eng. Pat. 23969. 1895.

feet will contain about 23,000 small pots, 20 tons of dilute acid and 80 tons of bark; the bark contains 50–65 p.c. of water. Altogether, about 30 tons of water are evaporated, along with $\frac{3}{4}$ ton of absolute acetic acid.

THE CHAMBER PROCESS

This has been developed chiefly in Germany and is there used extensively. In this country, Cookson's Chamber Process, modelled on the German, is in operation on the Tyne. The outstanding differences between the chamber and the stack processes are that tan is dispensed with as a source of heat and carbon dioxide; all the necessary materials are passed into the corroding chambers in regulated quantities and very thorough control of temperature and other factors is possible.

The corroding chambers are built of brick and are about 24 feet high and 20–25 feet square. The gases are generated beneath the chambers and enter them through pipes in the floor; at the top of the chambers there are openings for ventilation which can be closed, if necessary, by wooden plugs. Air is admitted through the sides of the chamber, near the base. The general arrangement is shown diagrammatically in Fig. 38.

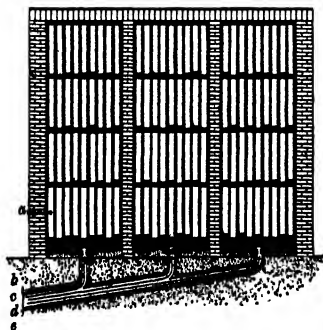


Fig. 38.—The Chamber Process (diagrammatic).

a, Straps of lead; *b*, Carbonic acid gas; *c*, Oxygen; *d*, Water vapour; *e*, Acetic acid vapour.

The refined lead for corrosion is cast into straps, without perforations, thinner than those used in the stack process and weighing 2.5—5 lbs. each: these are slung over sticks which are carried on arches. The total weight of lead set in an average chamber is 45—55 tons. Carbon dioxide is generated by burning weighed quantities of coke, of known composition, the weight of carbon burnt being only slightly in excess of the amount eventually contained in the white lead, reckoning on an average corrosion. Water and acetic acid are evaporated in fire-heated copper pots, somewhat more acid being used than in the stack process. The use of a separate evaporator for acetic acid may be avoided by allowing the acid to drip from a funnel into one of the hot flues leading into the chamber. The amount of water used is 60—100 gallons a day. The temperature is 55°—70° C., and the heat is supplied by the hot gases, supplemented to some extent by the heat of chemical action. In starting operations and for about a week, stronger acid is used than in the later stages of the process. In general, acid is added every day during the course of the process. Carbon dioxide is admitted when drops of basic acetate solution appear on the straps and the gases are regulated to maintain these in a damp condition.

The time of corrosion is from 42 to 60 days, and the proportion of the lead corroded is greater than in the stack process, amounting to 80—90 p.c.; it depends on the size and weight of the straps and on the quantity of lead set in each height. Before stripping, the chambers are thoroughly drenched with water, by means of special sprays, placed in the ventilating holes. The corruptions are taken to the dollies and grinding mills and treated in much the same manner as the stack product. The pulp from the settling tanks is filtered, pressed, then dried in ovens, the shelves of which are jacketed for heating purposes.

The following analyses of chamber gases are averages, over a long period, for two chambers:

| | 1. | 2. |
|----------------------|------|------|
| Oxygen | 14'0 | 15'4 |
| Carbon dioxide . . . | 0'67 | 0'24 |

These figures are instructive as showing the extent to which atmospheric oxygen is absorbed in the process. This point may be emphasized by a simple calculation. Suppose that 50 tons of lead are set in a chamber 25 feet cube and that 60 p.c. is corroded in 60 days, the average temperature being 60° C.; then the weight of atmospheric oxygen absorbed is 2·3 tons, which occupies 62,300 cubic feet at 60°. The absorption of oxygen is thus, in round numbers, 1000 cubic feet a day, which is equivalent to one-third of the total volume of the chamber. The atmosphere of the chambers is saturated with water vapour. The pressure of this at 60° is 150 mm., so that the gases contain 20 p.c. of water vapour.

One great merit of the chamber process lies in the control which can be exercised over the temperature and the composition of the reacting gases. The spaciousness of the chambers is possibly also an advantage, since it favours the convection and diffusion of the gases and the establishment of uniform composition. The absence of dirty bark and coloured drippings results in the white lead being cleaner than that produced in the stacks. Comparison of the two products shows the stack white lead to have a pronounced grey colour, whereas the chamber product is pure white. By selection of the composition of the reacting gases, a corroder can naturally cause the composition of the white lead to vary within wide limits; actually, he works for a product of uniform composition. An average analysis shows: $\text{PbO} = 86\cdot4$; $\text{CO}_2 = 11\cdot3$; $\text{H}_2\text{O} = 2\cdot3$ p.c., which corresponds closely with the formula $3\text{PbO}, 2\text{CO}_2, \text{H}_2\text{O}$ (calculated: $\text{PbO} = 86\cdot3$; $\text{CO}_2 = 11\cdot4$; $\text{H}_2\text{O} = 2\cdot3$). For similar grades of fineness, the amount of 'coarse' (normal) carbonate, insoluble in dilute acetic acid of the same strength is only 0·1 to 0·3 p.c. for the chamber white lead, but it varies from 6 to 20 p.c. for the stack white lead. The

following figures, which are averages over a long period, illustrate this difference of carbonation in the two processes:

| Molecular ratios | Chamber white lead | Stack white lead | |
|----------------------------------|--------------------|--------------------------|-----------------------|
| | <i>x</i> | Ordinary run <i>x</i> | Short run <i>x</i> |
| $x\text{PbCO}_3:\text{Pb(OH)}_2$ | 1.88 to 2.56 | 2.22 to 2.72 | 2.07 |

The greater extent of carbonation of the stack product is thus clearly shown. When the stack is worked on a short run (about half the normal), the carbonation is not so pronounced and the white lead approximates in character and composition to the chamber product.

THE CHEMISTRY OF CORROSION

Some doubt prevails on many of the fundamental chemical changes which take place in the formation of white lead by the corrosion-process. It has already been noted that white lead is not a pure substance, in the chemical sense, but a commercial preparation, which may vary within fairly wide limits. It is a fact, however, that it can be produced continuously, on a large scale, with a composition approximating to that of a hydrated basic carbonate of lead of the formula $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$, otherwise written, and preferably so in view of the confusion still current on this subject, on an analytical basis, as $3\text{PbO} \cdot 2\text{CO}_2 \cdot \text{H}_2\text{O}$.¹)

The grounds for the belief that this compound exists have already been given; there is no certain evidence of the

¹ The old idea that white lead is a mixture of lead hydroxide and lead carbonate is still encountered, though it has long been proved to be erroneous. Analyses are, however, usually expressed in terms of these two compounds and this method will sometimes be adopted in the following pages, but without the implication that the combined water is present as lead hydroxide, or the carbon dioxide entirely as normal carbonate. It is hardly necessary to add that the alternative formula does not connote that white lead contains litharge, carbon dioxide and water.

existence of other basic carbonates, though such might be expected, since lead forms basic salts with great facility, and the excellent characterisation of many of these, e.g. the basic chlorides, which occur naturally as the minerals matlockite, mendipite and laurionite, leaves no doubt as to their composition. It is generally accepted that the basic carbonate, mentioned above, occurs to a greater or less extent in white lead, the main arguments being, apparently, the coincidence in composition and the general resemblance of white lead to the basic carbonates produced by laboratory methods. Admitting that white lead does contain this basic carbonate, it must be borne in mind that the latter is always associated with normal lead carbonate, possibly also with one or more other basic carbonates and, in extreme cases, even with lead hydroxide. No method of separating any constituent from white lead, except the normal carbonate, has yet been devised.

Many suggestions for a more descriptive name for the basic carbonate have been made, examples of which are hydroxy-carbonate of lead, and lead mono-hydrate carbonate, but it may be urged that any attempt at greater precision of nomenclature is premature, and that a name, admittedly somewhat vague, is better than one which implies a knowledge of composition or constitution which we do not possess. To apply such names to white lead itself is obviously absurd. The expression, commonly encountered, that a certain white lead has "the theoretical composition", epitomises some of the loose views held on this subject, and it is to be understood as meaning, in reality, nothing more than that the sample in question yields the same results on analysis, as would a basic carbonate of the formula $3\text{PbO} \cdot 2\text{CO}_2 \cdot \text{H}_2\text{O}$.

In actual practice, the composition of white lead varies considerably. In the table below are given some analyses of Stack and Chamber white leads, and for comparison the values calculated for several (possible) hydrated basic carbonates, and for the normal carbonate of lead. The figures for PbCO_3 and Pb(OH)_2 , in the last two lines, are calculated from the proportions of carbon dioxide and water.

| | Stack White Lead | | Chamber White Lead | | $2 \text{ PbO} \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$ or $\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ | $3 \text{ PbO} \cdot 2 \text{ CO}_2 \cdot \text{H}_2\text{O}$ or $2 \text{ PbCO}_3 \cdot \text{Pb(OH)}_2$ | $4 \text{ PbO} \cdot 3 \text{ CO}_2 \cdot \text{H}_2\text{O}$ or $3 \text{ PbCO}_3 \cdot \text{Pb(OH)}_2$ | $\text{PbO} \cdot \text{CO}_2$ or PbCO_3 |
|------------------------|------------------|-------|--------------------|-------|---|---|---|---|
| | 1. | 2. | 1. | 2. | | | | |
| PbO . . . | 85.75 | 86.10 | 86.45 | 86.30 | 87.80 | 86.33 | 85.61 | 83.52 |
| CO ₂ . . . | 12.40 | 11.75 | 11.15 | 11.54 | 8.65 | 11.35 | 12.66 | 16.48 |
| H ₂ O . . . | 1.85 | 2.15 | 2.40 | 2.10 | 3.55 | 2.32 | 1.73 | — |
| PbCO ₃ . | 75.39 | 71.20 | 67.70 | 70.06 | 52.55 | 68.90 | 76.86 | 100 |
| Pb(OH) ₂ | 24.80 | 28.81 | 32.30 | 28.14 | 47.45 | 31.10 | 23.14 | — |

These figures represent the products of one firm. Variations are naturally greater when white leads of various makes are considered. The carbon dioxide then generally lies, according to Klein, between 11.8 and 12.5 p.c., though some makers turn out material of good quality, containing as much as 14 p.c. of carbon dioxide and, on the other hand, white leads are on the market, which contain much less carbon dioxide than 11.35 p.c., the amount corresponding to the basic carbonate postulated as the basis of white lead. Normally, the stack lead contains 0.8 p.c. more carbon dioxide than the chamber lead. A specification of the St. Louis and San Francisco Railroad Co. states that the composition of white lead must lie between the limits $\text{PbCO}_3 = 67$ to 80 p.c., $\text{Pb(OH)}_2 = 32$ to 20 p.c.¹) This will suffice to illustrate the wide range permissible in the composition of the material, consistent with suitable properties when it is employed as a pigment.

To prevent misconception, the two main points so far dealt with may be summarised. Though there is no clear proof, it is possible, or even probable, that white lead of good quality contains a basic carbonate, identical with one prepared in the laboratory, which corresponds in composition to the formula $3\text{PbO} \cdot 2\text{CO}_2 \cdot \text{H}_2\text{O}$. The amount of this compound present varies within wide limits, for it is almost invariably,

¹ Quoted by Holley, *op. cit.*, 142.

if not always, mixed with normal carbonate, and there may also be present other basic carbonates and even lead hydroxide. It will be assumed in the sequel that this basic carbonate is an essential product of the process of corrosion. Considered as a pigment, the quality of white lead is not uniquely dependent on its composition; considerable variation is allowable and it by no means follows that a product agreeing closely in composition to the known basic carbonate is a desirable one. In other words, the physical nature of the preparation has an influence on its properties as a pigment, at least as great as its chemical composition.

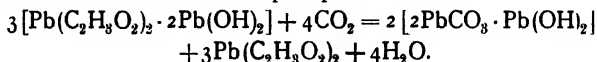
Turning now more particularly to the chemical changes involved in the production of white lead; it may be noted that many important processes depend on the direct carbonation of hydrated oxides of lead. As similar results are obtained by the carbonation of basic salts of lead, and as the ratio of normal salt to oxide or hydroxide of lead varies considerably in the various processes, it is evident that the composition of the precipitated basic carbonate is independent of the degree of basicity of the salt which is used. Virtually, then, in such cases, one is dealing with a solution of lead hydroxide which, being thrown out of solution by carbonic acid, leaves the normal salt free to dissolve more oxide or hydroxide of lead. This is essentially the catalytic view of the process, propounded by Liebig and Hochstetter¹) in 1837, and extensively adopted, though with minor, and sometimes not very plausible, alterations.

The general sequence of reactions in the corroding chamber is recognised to be as follows. Lead is oxidised by atmospheric oxygen, in presence of water, and converted into the hydroxide; this is neutralised by acetic acid and the resulting normal acetate dissolves lead hydroxide and is converted thereby into the basic acetate. This last then reacts with carbon dioxide, with formation of basic carbonate of lead and regeneration of normal lead acetate, which acts as

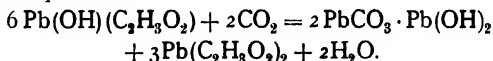
¹ Liebig's *Handbuch der reinen und angewandten Chemie*, 1837, p. 831.

a solvent for more lead hydroxide and thus furnishes fresh material for the production of basic carbonate.

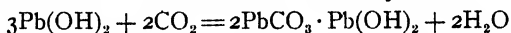
Liebig and Hochstetter assumed that the basic acetate in question had the formula, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{Pb}(\text{OH})_2$ and formulated the reaction of precipitation thus:—



Others, postulating a less basic acetate, derive a slightly different equation.—



As the capacity of lead acetate solution to dissolve lead oxide increases very much with dilution, reaching a limit at extreme dilution, in which 10 equivalents of oxide dissolve in 1 of acetate, it is highly probable that, even if the acetates formulated above are concerned in the reaction, they are by no means the only ones; or, alternatively, that the function of the lead acetate is merely that of a solvent, and that the essential reaction is carbonation of lead hydroxide.



Whatever view be taken, it is evident that none of these equations can fully represent the reactions which occur in stack and chamber; there are several subsidiary reactions, some of which are reversible, and though it is impossible to state their exact influence on the production of the basic carbonate, their effect on the degradation of this into normal or coarse carbonate can be more certainly inferred.

During active corrosion, there is a steady flow of lead hydroxide, derived by the oxidation of the lead, into the reacting system. This is converted, as we have seen, successively into acetate, basic acetate and basic carbonate of lead, by the agency of acetic and carbonic acids. Both basic acetate and basic carbonate are open to the attack of acetic acid, the reaction resulting, in each case, in the formation of normal acetate, and this compound reacts with carbon dioxide, even in presence of acetic acid of normal strength, yielding thereby acetic acid and normal lead carbonate. This last

compound is also produced by the action of carbon dioxide on the basic carbonate of lead. The probability of the bicarbonate of lead playing any part in the process is remote, and lead acetate solution has no effect on the basic carbonate of lead, though the nitrate dissolves it with formation of basic nitrate.¹⁾

Now it is evident that the chief controlling factors during active corrosion are the rate of feed of lead hydroxide, which is determined by the velocity of oxidation of the lead, and the amount and relative proportions of the two acids concerned in the process. When the correct balance is maintained, then the production and relative permanence of the basic carbonate is favoured, and it may be inferred that the inflow of lead hydroxide is sufficient to keep the concentration of acetic acid in the liquid, condensed on the surface of the metal, low, and concurrently, to convert any normal acetate, produced by the action of acetic acid on hydroxide, basic acetate, basic or normal carbonate of lead, immediately into basic acetate. The presence of carbonic acid ensures the conversion of this into basic carbonate, whence it appears possible that the basic carbonate may constantly undergo partial dissolution and precipitation, so that its apparent permanency, in presence of acetic acid, is illusory.

Any disturbance of the correct balance between the quantities of reacting materials results in "accidents to the work", as Vernatti puts it, or is reflected in the changed composition of the corrosions. The disappearance of the lead core, for example, is speedily followed by the conversion of the corrosions into normal carbonate; in other words, degeneration of the basic carbonate ensues, since the feed of lead hydroxide is cut off and the basic lead compounds are converted into normal acetate, and normal carbonate is precipitated from this. The liquid which is condensed on the lead straps in the chamber-process and drips from these is likewise deprived of lead hydroxide and is found, in accordance, to

1 M. A. Levol, *Ann. Chim. Phys.*, 1840, 75, 108.

contain only normal acetate of lead; and in the stack process, bunches of uncorroded lead, which occur in places where condensation is excessive, usually overlie pots, full, at the end of the process, with solution of normal acetate of lead.¹⁾ There are, however, cases where lead resists corrosion from no ascertainable cause.

If oxidation of lead preponderates, then the corruptions contain, probably, lead hydroxide, and the carbon dioxide content of the white lead is low. This last, coupled with the impossibility of separating hydroxide from basic carbonate, may afford an alternative explanation to the view that basic carbonates of the type $\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ are first formed in the corrosion-process. Incidentally, it is evident that corruptions in general are not uniform in composition, since the alkaline hydroxide is concentrated next to the metal, and the acids on the outside, and the rate of diffusion is probably slow. It is not uncommon to find many times as much sandy (normal) carbonate on the outside of a corrosion as on the inside.

That such a balance, as has been described above, with resultant uniformity in the composition of the white lead, is attainable in the chamber process is not surprising, considering the control of conditions which is possible. A moment's consideration will, however, show that the stack process is not so inferior in that respect: there is some measure of automatic regulation here, since the generation of heat and of carbon dioxide depend upon the fermentation of the tan. But the vaporisation of the water and acetic acid depend also on the temperature, and this factor controls the ventilation of the stack and thus the amount of atmospheric oxygen

1 During the early stages of the development of the Chamber process in this country, the white lead from a chamber, where the conditions were abnormal, had the composition: $\text{PbO}=83.85$, $\text{CO}_2=15.70$, $\text{H}_2\text{O}=0.45$ p.c. or, otherwise expressed, $\text{PbCO}_3=94.1$, $\text{Pb(OH)}_2=5.9$ p.c. These figures illustrate well the effect of the disturbance of the correct balance of the reacting materials on the composition of the product.

available for the oxidation of the lead. Thus the concentration of all the reacting gaseous materials, in all probability, increases and decreases *pari passu*, until at any rate the acetic acid has all been driven out of the stack. True corrosion then ceases. Further reactions are still possible, since the corrosions retain some acetate, but carbon dioxide is in excess and carbonation, or degeneration of the basic carbonate, then sets in, with the familiar result that the stack white lead is usually more carbonated than that from the chamber process, in which the feed of acetic acid is kept up to the end of the process. The effect of a short run in the stack process is to cut down, or even eliminate, the period of degeneration, and the white lead then produced contains less carbon dioxide, as shown in the table on p. 264, and approximates in composition to the chamber product, as ordinarily prepared. It may be added that the control of the chamber process is such that a corroder can make, within limits, a white lead of any composition, and that the illustrative analyses, already quoted, refer to products prepared with a view to their commercial value and, therefore, free from undue excess of coarse or normal carbonate.

The crude corrosions, as lifted from the stacks and chambers, are admittedly heterogeneous. In their conversion into white lead by the grinding and washing processes, very intimate blending of the constituents is naturally effected and the soluble lead acetate and free acetic acid are removed, along with such adventitious impurities as tan, etc. At the same time minor chemical changes take place. Some blue lead, introduced into the mixture during grinding, is oxidised and carbonated: acetate in solution is precipitated by sodium carbonate, and both of these processes result in the addition of basic carbonate of lead to the main bulk of the material. A similar effect would also be produced if the corrosions contained lead hydroxide. The general result of these processes is, therefore, to increase the amount of basic carbonate, to eliminate soluble substances, and to produce an exceedingly intimate mixture of the constituents.

THE ROWLEY OR MILD PROCESS

The lead used in this process need not be of a high degree of purity, provided it contains less than 1 oz. of silver per ton. It is melted in kettles holding 2 tons, run off through a heated pipe in the bottom and comminuted by being brought into contact with a jet of steam, heated above the melting point of the metal. The blast is directed downwards and the operation is carried out in a large iron vessel, the bottom of which is covered with water 2 feet deep. The metal sludge is withdrawn from this, by means of drag and screw conveyors to float-boxes and is discharged thence to the vessels in which it is oxidised. These hold from 3 to 4 tons of metal and in them the sludge is agitated and subjected to a blast of low pressure air for 24—36 hours; at the end of this time, about 80 p.c. of the metal has become converted into a mass of hydrated oxides, presumably containing sub-oxide, of a greenish-yellow to brownish-orange colour. The oxides are then floated off and the unaltered lead returned to the oxidisers.

The oxides are then thinned with water and brought into wooden cylinders, smaller than the oxidisers, where they are agitated and exposed to a stream of carbon dioxide. The gas is produced in coke-furnaces; it is scrubbed and cooled and contains up to 19 p.c. of carbon dioxide and is free from carbon monoxide and sulphur dioxide. No change is apparent in the carbonation for 18 hours, but at the end of this time, a considerable expansion in volume sets in, attended by hydration and rapid absorption of carbon dioxide. Fresh water is added at this stage; the temperature varies from 15° to 50° and the completion of the carbonation is effected in 36 hours.

The white lead produced in this process is pure, of uniform grain and requires neither grinding nor washing. It is uniform in composition, corresponding to the formula $3\text{PbO} \cdot 2\text{CO}_2 \cdot \text{H}_2\text{O}$ and furnishes a satisfactory paint, easily worked under the brush.¹⁾ The various operations are easily controlled,

¹⁾ C. D. Holley, *Journ. Soc. Chem. Ind.*, 1909, 28, 403.

hand-labour is brought down to a minimum, and there is much to recommend in the method from the hygienic point of view, since handling of the material is avoided from the time the lead is melted down, until the white lead leaves the plant. Chemically speaking, the process has many features of interest. The somewhat vague term 'mild', applied to it, indicates the absence of acetic acid, and, in fact, assuming the product to be largely a definite basic carbonate, of the formula given above, the process almost realises the synthesis of that compound from its proximate constituents.

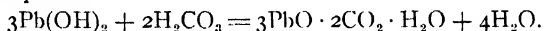
THE BISCHOF OR BRIMSDOWN PROCESS

The white lead prepared by the Brimsdown Lead Co., Middlesex, has an established position in the English market and the chemical methods employed in its manufacture are of considerable interest, especially when considered in conjunction with those of the Rowley process. The main stages in the operation are as follows: Litharge, prepared in reverberatory furnaces, is ground finely and then reduced by water-gas at a low temperature (250—300°). The sub-oxide thus produced is carried by closed conveyors to the hydrating pans, where it is mixed with a measured amount of water, agitated by stirrers and exposed to a current of air until the sub-oxide is oxidised and hydrated. Enough water is now added to form a thick paste, together, apparently, with a little lead acetate, and this is carbonated for about 24 hours. The process is hygienic and susceptible of thorough control.¹⁾

One chemical feature common to this and the Rowley process is the production of hydrated monoxide of lead by methods other than precipitation or oxidation of the metal. This is achieved by utilising the spontaneous (and exothermal) reaction of oxidation and hydration, which the sub-oxide of lead undergoes when exposed to air in a moist condition. There is a lack of precise information concerning these reac-

¹ The author understands that this process has been simplified in recent years; no information on the subject is available.

tions, for little is known of the chemical properties of the sub-oxide, but the interesting fact is recorded by Holley (*op. cit.*) that in the Rowley process, only one third of the total hydration, which the lead undergoes in its conversion into white lead, is accomplished during the hydration-stage, the remainder occurring during carbonation and being accompanied by a considerable increase in bulk of the material affected. This behaviour suggests that the formation of the basic carbonate is not so simple a process as represented by the equation:



Initial formation of normal carbonate, or of a more basic carbonate than is assumed to be present in the end-product, would not facilitate the explanation; but the production of a hydrated carbonate, such as the bi-carbonate, $\text{PbO} \cdot 2\text{CO}_2 \cdot \text{H}_2\text{O}$ followed by the immediate reaction of this with lead monoxide, would give some clue to the phenomenon of simultaneous hydration and carbonation.¹)

Properties of White Lead.—Commercial white leads are not of uniform composition and they vary a good deal with respect to those important properties upon which their use as a pigment depends. Such variations are, however, not uniquely connected with composition; they depend also on the fineness and uniformity of grain, on the presence of normal lead carbonate and, possibly, on many other conditions. A sample of 'theoretical' composition is not necessarily the best in actual practice. It seems to be admitted, however, that the carbon dioxide should fall between 11 and 13 p.c., otherwise the white lead is defective as a pigment.

So far as it is possible to generalise on a product which is not uniform, it may be stated that white lead is amorphous,

¹ The work of W. A. Davis (*Journ. Soc. Chem. Ind.* 1906, 788) on the basic carbonates of magnesium is suggestive in connection with the problems of white lead formation. This author shows, among other things, that magnesium bicarbonate suffers decomposition, in warm solution, yielding a crystalline, hydrated, basic carbonate of magnesium.

of sp.gr. 6.81,¹⁾ and it loses water completely at 150°, without parting with carbon dioxide. The grain depends on the method of preparation and the grinding. The grains of mild white lead are uniform in size, whereas those from material prepared by the stack process vary in diameter from 0.00002 to 0.00026 inch.

Difference in the size of the grains is held by many to be an advantage, since it allows of the grains being more closely packed and produces a surface with the smallest number of voids.²⁾ Probably all samples contain crystalline normal lead carbonate, some of which is left as residue when the white lead is treated with dilute acetic acid. The analysis of such a residue from the chamber lead shows it to consist essentially of lead carbonate:

| | |
|-----------------------------------|-------------|
| PbCO ₃ | 97.81 p.c. |
| PbSO ₄ | 0.84 „ |
| CaCO ₃ } | 0.97 „ |
| FeC ₂ O ₄ } | |
| SiO ₂ | 0.34 „ |
| Organic matter | 0.11 „ |
| | 100.07 p.c. |

It is generally admitted that this crystalline carbonate is useless as a pigment. In contradistinction to the basic carbonate it is crystalline and transparent. It is possible that all forms of normal carbonate are not quite valueless as a pigment, for there is a difference in physical properties between that which is precipitated from solution and that produced slowly by the degeneration of the basic carbonate. According to Holley, it is rare to find crystalline carbonate in a white lead, which shows less than the 'theoretical' amount of carbonate.

Much controversy has arisen with regard to the changes which take place when white lead is ground with linseed oil, the main issue being whether hydrolysis of the oil takes place

1 H. A. Gardner, *Papers on Paint and Varnish*. 1920, p 257.

2 G. W. Thompson, *Journ. Soc. Chem. Ind.*, 1909. 28, 406.

or not. If any particular preparation of white lead contained lead hydroxide, it would be natural to expect hydrolysis or saponification; but if it consisted of a mixture of normal and basic carbonates of lead, there would be no reason *a priori* to anticipate such a reaction. The experimental work of Davis and Klein¹) has shown that lead soaps are indeed formed from white lead and linseed oil, and that some of these are insoluble and others soluble in ether, but these authors ascribe their formation entirely to reaction of the white lead with the free fatty acids present in the oil. The evidence is against saponification; in any case, very small amounts of lead soaps are formed. On the old erroneous view, not yet extinct, that the carbonate gave body to the paint and the hydroxide saponified the oil, white lead should saponify about 76 p.c. of its weight of oil. An ordinary oil paste containing 10 p.c. of oil, however, only retains about 0.2 p.c. of oil after extraction with ether or light petroleum.

White lead is discoloured by hydrogen sulphide, owing to the formation of black lead sulphide, but such discoloration is uncommon. When used as a paint, it has a tendency to become granular, but such 'chalking' or 'flouring' as it is termed, leave the surface in a good condition for repainting. The cause of chalking is obscure and has been variously traced to the presence of fatty acids in the oil, over-heating during grinding, and the presence of lead acetate in the white lead.²)

WHITE LEAD SUBSTITUTES

'Genuine' brands of white lead are pure in England; adulteration of white lead with barium sulphate is recognised both by manufacturers and merchants, and such mixtures are known as 'reduced' white leads. Of substitutes proper, some have been designed with the object of eliminating altogether a material, the production and utilisation of which was ac-

¹ *Journ. Soc. Chem. Ind.*, 1907, 26.

² Holley, *Zinc and Lead Pigments*.

accompanied by poisoning of the work folk and replacing it by one alleged, though often on very flimsy grounds, to be non-poisonous; others have been developed simply on a chemical and economic basis.

The basic chloride is now of historical interest only, its manufacture having been patented by Pattinson in 1849 and abandoned after some years' trial. It was prepared from galena, by converting this into the chloride with hydrochloric acid and precipitating the solution of lead chloride with half its equivalent of lime. The basic chloride has the same composition as the mineral laurionite, PbO , PbCl_2 , H_2O .

Freeman's so-called *Innocuous White Lead* consists to a large extent of precipitated sulphate. Lead splashes are converted into acetate by the agency of acetic acid and air; from the acetate solution, the sulphate is precipitated by means of sulphuric acid and is incorporated with 20 p.c. of zinc oxide and a little barium sulphate.¹⁾

Sublimed White Lead is also a sulphate and supposed to be non-poisonous. It was introduced by Bartlett in 1866 and is sometimes known by this name, or by those of Lewis and Bartlett. As in the preparation of Pattinson's white lead, the raw material is galena; this is smelted under such conditions that a large amount of fume is produced; and the complete oxidation of this yields a very fine powder containing, possibly, a basic sulphate of lead, or a very intimate mixture of oxide and sulphate, along with zinc oxide in relatively small quantity. This process was worked in Bristol in 1886, a Jumbo furnace being used.²⁾ The pigment has been made in this country by the Purex Lead Co. and by Briton's Sulphate Co.

In the United States, at Joplin and St. Louis, a water-jacketed slag-eye furnace is employed. The fuel is coke and the charge consists of galena concentrates, grey slag, burnt fume and carbonate ore, along with fluxing materials in the form of iron, ferruginous slags and limestone. These are

1 A. P. Laurie, *Journ. Soc. Arts*, 1894, **42**, 133.

2 P. F. Nursey, *Journ. Soc. Arts*, 1893, **41**, 445; L. T. Hughes, *Journ. Soc. Chem. Ind.*, 1909, **28**, 415.

fed in through a door above the jackets and lead and slag flow away continuously into a forehearth, from which the slag overflows and is granulated and washed to recover shots of metal. The fume and dust pass into a large combustion chamber, where the complete oxidation of volatilised sulphide and other combustible substances is effected, thence into a cooling tower, and from there into a row of goose-necks, 25 feet high and 44 inches in diameter and finally into a bag-house.¹⁾

A nice adjustment of working conditions is necessary to obtain a satisfactory pigment. The slag must flow freely and the air, supplied by the tuyeres and drawn into the combustion chamber through the feed-door, must be carefully regulated. The addition of the smelting materials requires to be skilfully performed. A modification of this process was worked by Hannay at Glasgow in 1892, the fume being precipitated with steam and the sludge washed with sulphuric acid and water.

The pigment contains 75—90 p.c. of lead sulphate, and 25—10 p.c. of lead oxide, and usually, too, 2—5 p.c. of zinc oxide; it should not contain more than 1 p.c. of zinc sulphate. It is very fine-grained, the particles averaging 0.00003 inch in diameter, and its sp.gr. is 6.2; it requires careful grinding to take the oil and is improved by the addition of 10—15 p.c. of asbestos, silica or Dutch white lead; it is stated to equal true white lead in colour, covering power and permanency.²⁾ As usually made, however, it is not equal to white lead in colour.

In the United States, the Bartlett process is also used for the treatment of complex sulphide ores of copper, lead, zinc and iron, which are of low grade, but carry some precious metal. The volatile lead and zinc compounds pass into the fume, which is oxidised in a combustion chamber and filtered in bag-houses. This fume is afterwards calcined and the resulting pigment, known as lead zinc white, contains about equal proportions by weight of lead sulphate and zinc oxide.

¹ Hofman, *Metallurgy of Lead*, p. 121.

² Hughes, *op. cit.*

The precious metals are assembled in a matte and the gangue is slagged.¹)

CHAPTER XII

OTHER COMPOUNDS OF LEAD

The compounds of lead, like the metal itself are distinguished by their great density, the specific gravities of some of the common derivatives being: $\text{PbO} = 9.4$; $\text{PbO}_2 = 9.4$; $\text{Pb}_2\text{O}_4 = 9.1$; $\text{PbS} = 7.5$; $\text{PbCO}_3 = 6.5$; $\text{PbSO}_4 = 6.2$; $\text{PbBr}_2 = 6.6$; $\text{PbI}_2 = 6.1$; $\text{PbCl}_2 = 5.8$; $\text{Pb}(\text{NO}_3)_2 = 4.5$. Most of them are insoluble in water, and indeed, of the commonly occurring compounds, only the nitrate and acetate are readily soluble in cold water. From the chemical point of view, one of the most striking properties of lead is its ability to form basic salts, some of which, especially those occurring naturally, are well characterised; many double salts with different acid radicles also exist.

The salts of lead are derived from the three oxides. Pb_2O , PbO , and PbO_2 . Those of the first type, the sub-salts, are not numerous and are difficult to prepare and not very stable, as they tend to decomposition, with production of salts of the second type and metallic lead. There is no evidence concerning the molecular formulae of these sub-salts. The typical salts of lead are derived from the monoxide and one of these, the chloride, is volatile and its vapour density corresponds to the formula PbCl_2 . In this case, then, the lead is bivalent and it may be assumed that other compounds of this type contain also the metal in the bivalent condition. Derivatives of lead dioxide are few and lack stability, but some of the organo-metallic compounds are stable and easily volatilised, and the determination of their vapour densities proves that the metal, in such combinations, assumes the quadrivalency to be expected from the position of lead in the periodic classification. Lead alkyl compounds of bivalent type are not easily formed, for in the interaction of zinc methide

¹ Holley, *The Lead and Zinc Pigments*, p. 188.

and lead chloride, lead is separated and only the tetramethide of lead is produced. The recent isolation of highly unsaturated compounds like the lead tricyclohexyl, $\text{Pb}(\text{C}_6\text{H}_{11})_3$, the molecular weight of which, determined cryoscopically, is in accordance with the formula just given, is of considerable interest, as showing that lead can form tervalent compounds, corresponding to the sesquioxide; no salts of this type have yet been prepared.

In the following account of those lead compounds, which have not already been described in sufficient detail, the classification adopted will be based on the important non-metallic element with which the lead is combined, the order being: the halogens, sulphur group, nitrogen group, silicon, boron and carbon, and finally, the lead salts of the acid-forming metallic oxides will be described. The salts containing different acid radicles and the basic salts will be considered separately.

Paneth and Nörring¹⁾ have indicated the existence of a gaseous *lead hydride*, obtained by the action of dilute hydrochloric acid on an alloy of bismuth and radio-lead (thorium B). The lead hydride could not be obtained by the action of acids on ordinary lead-magnesium alloys, but traces were formed by a combined electrolysis-spark process. These observations bring lead into line with the other members of the fourth group, germanium and tin. The composition of the hydride is as yet unknown, but as the evidence in the case of germanium points to a tetrahydride, it is probable that lead, in its hydride, assumes the quadrivalency characteristic of its compounds with the hydrocarbon radicles.

HALOGEN COMPOUNDS OF LEAD

The three *sub-halides* have been prepared by heating plumbous oxide in the vapour of the alkyl halides; the chloride at 311° , the bromide at 261° , the iodide at 262° . The first two are grey and the iodide is a bright yellow powder. They

¹ Ber. 1920, **53**, 1693.

are all difficult to prepare, requiring definite conditions and the maintenance of temperature and pressure within narrow limits. They are oxidised by air, especially when moist, and are decomposed into metal and normal halide when heated above their temperature of formation, or when brought into contact with acids. They are much less soluble than the normal halides, the solubility-data in milli-equivalents per litre at 25° being: PbCl_2 , 2.2; PbBr_2 , 0.4; PbI_2 , 0.17.¹⁾

Lead chloride (horn lead, plumbum corneum) PbCl_2 occurs native in the craters of volcanoes as the mineral *cotunnite*, and may be prepared readily by treating the oxide or carbonate with hydrochloric acid, or by precipitating a fairly concentrated solution of a lead salt with a soluble chloride. On a large scale it may be prepared by heating litharge with a slight excess of hydrochloric acid at 200° and 25 atmos. pressure, in an autoclave lined with an acid-resisting material.²⁾ In a colloidal form it can be obtained by mixing together lead acetate, or the lead salt of any other organic acid, with an alkali, or alkali earth chloride.³⁾

Lead chloride forms a white crystalline precipitate or white silky, rhombic needles of sp.gr. 5.8. When heated in absence of air it melts at 495°, and boils at 945° at 754 mm.; its vapour density is 9.64 (air = 1) at 1070°, corresponding to the molecular formula PbCl_2 .⁴⁾ The heat of vaporisation at m.p. is 40,600 cal. It is less soluble in dilute hydrochloric acid and in solutions of chlorides than in water, but dissolves more readily in concentrated hydrochloric acid.⁵⁾ The solubility is at a minimum when there is 10 p.c. of hydrochloric acid in the solution. The solubility of the salt in water at various temperatures is given in the following table:

1 H. G. Denham, *Journ. Chem. Soc.* 1917, **111**, 29; 1918, **113**, 249.

2 Eng. Pat. 12953, 1895; see also Eng. Pats. 16213, 1889; 8914, 1895; *Journ. Soc. Chem. Ind.* 1890, 941; *ibid.* 1895, 873; *ibid.* 1899, 357.

3 van de Velde, *Chem. Zeit.* **17**, 1908.

4 A. Scott, *Proc. Roy. Soc. Edin.*, 1887, 410.

5 André, *Compt. rend.*, 1883, **97**, 1302; Lichy, *Journ. Amer. Chem. Soc.*, 1903, **25**, 469.

| Temperature (0°C.) | 0° | 15° | 25° | 35° | 55° | 80° | 95° |
|--|--------|--------|--------|--------|--------|--------|--------|
| Grams of PbCl_2 in 100 gms. water . | 0.6728 | 0.9090 | 1.0842 | 1.3244 | 1.8263 | 2.6224 | 3.1654 |

The solubility in hydrochloric acid, of various strengths, at 0° is:

| Grams HCl per litre . | 0 | 1 | 10 | 100 | 200 | 250 | 300 | 400 |
|---------------------------------|------|-----|-----|-----|-----|------|------|------|
| Grams PbCl_2 per litre | 5.83 | 3.6 | 1.2 | 1.2 | 5.2 | 10.5 | 17.5 | 40.0 |

Lead chloride suffers slight hydrolysis in water, namely, to the extent of 0.6 p.c. at 100°, when 1 gm.mol. is dissolved in 100 litres.¹⁾

Many double salts of lead chloride and other chlorides have been prepared by bringing together aqueous solutions of their constituents; the following may be quoted as examples: $\text{PbCl}_2 \cdot 2\text{NH}_4\text{Cl}$; $2\text{PbCl}_2 \cdot \text{RbCl}$; $\text{PbCl}_2 \cdot 4\text{CsCl}$; $\text{PbCl}_2 \cdot \text{BaCl}_2$.

Lead tetrachloride PbCl_4 may be formed by passing chlorine into lead chloride, suspended in concentrated hydrochloric acid at 10°—15°. On adding ammonium chloride, *ammonium plumbichloride* $(\text{NH}_4)_2\text{PbCl}_6$ separates.²⁾

When this ammonium compound is added, little by little, to ice-cold concentrated sulphuric acid, lead tetrachloride separates as a yellow, highly-refractive oily liquid, which fumes in air, smells like hypochlorous acid, and induces a sweet taste in the mouth. It has sp.gr. 3.183, is stable under sulphuric acid, but is liable to explode, especially when heated, forming chlorine and lead chloride. It solidifies at —15° to a transparent yellow crystalline mass. With hydrochloric acid it forms a crystalline compound H_2PbCl_6 , which dissolves, on further addition of acid, and is decomposed by water into lead dioxide and hydrochloric acid.³⁾ Many salts of this chlorplumbic acid

1 H. Ley, *Ber.*, 1898, **30**, 2194.

2 Hutchinson and Pollard, *Journ. Chem. Soc.* 1899, 212; Seyewetz and Trawitz, *Compt. rend.* 1903, **136**, 686; *Bull. Soc. chim.* [III], **29**, 261; Elbs and Nübling, *Zeitsch. Elektrochem.* 1903, **9**, 776.

3 Friedrich, *Monatsh.* 1893, **14**, 505; see also *Ber.* 1893, **26**, 1434; de Coninck, *Bull. Assoc. belge Chim.* 1902, **16**, 94.

have been prepared, some, like the potassium salt K_2PbCl_6 , in crystalline form. A great number of salts derived from organic bases are also known, for example, methylamine yields the compound $(CH_3NH_2)_2 \cdot H_2PbCl_6$ and ethylenediamine the compound $(C_2H_4NH_2)_2 \cdot H_2PbCl_6$. When these are well crystallised, regular and rhombic forms predominate. The chlorplumbates of pyridine and quinoline are stable. Solutions of these organic derivatives, when treated with ammonia, yield precipitates of lead peroxide; hydrogen peroxide reduces them to plumbous salts.¹⁾

Lead chlorite, chlorate, and perchlorate are also known, the first being prepared by double decomposition of a lead salt and sodium chlorite, the last two by dissolving lead monoxide in the corresponding acid. The chlorate is of some importance by reason of its use in the electrolytic refining of lead (q.v.) When heated, it yields a mixture of chlorine and oxygen and leaves a residue of lead chloride and lead peroxide. This is the result of two independent reactions, in one of which lead chloride and oxygen are produced, in the other, lead dioxide, chlorine and oxygen; secondary reaction between lead peroxide and chlorine yields lead chlorine and oxygen.²⁾

Lead bromide $PbBr_2$ is obtained by treating lead oxide with aqueous hydrobromic acid, or by precipitating a lead salt with a soluble bromide. It forms white shining needles, which darken when exposed to sunlight³⁾; sp.gr. 6.6. It resembles the chloride in properties and forms double bromides and oxybromides.

Lead iodide PbI_2 is formed by dissolving lead in hydriodic acid, or by precipitating the solution of a lead salt with a soluble iodide. It forms yellow crystals of sp.gr. 6.1, which on heating become yellowish-red, bright red, and finally brownish-black.

Lead iodide is soluble in potassium iodide owing to the formation of a double iodide, $KI \cdot PbI_2$, or $KPbI_3$. This can

1 A. Gutbier and M. Wissmüller, *Journ. pr. Chem.* 1914, **90**, 491.

2 Sodeau, *Journ. Chem. Soc.*, 1900, **77**, 717.

3 Norris, *Amer. Chem. Journ.* 1895, **17**, 189.

be isolated by crystallisation from the solution and when dissolved in dry acetone forms a colourless solution. If this solution be poured on filter paper and the solvent allowed to evaporate, the paper can be used as a delicate test for moisture, a mere trace of which turns it yellow.¹⁾ A saturated solution of lead iodide in potassium iodide is often used for the separation of heavy minerals from lighter spars; it is called Sonstadt's solution and its sp.gr. exceeds 3.

A periodide of lead and potassium is prepared by boiling 150 grams of potassium iodide, 4 grams of lead iodide, 70 grams of iodine and 90 c.c. of water. The solution is filtered and on cooling violet prisms are deposited of the composition $9\text{KI} \cdot 4\text{PbI}_2 \cdot \text{I}_2 \cdot 10\text{H}_2\text{O}$.²⁾

Lead fluoride PbF_2 is formed in the same way as the corresponding iodide. It is a white powder, almost insoluble in water and in hydrofluoric acid, but readily soluble in hydrochloric and in nitric acid. It yields a basic fluoride and a chlorofluoride.

Lead tetrafluoride PbF_4 is said to be formed in a colloidal state by the action of concentrated sulphuric acid on the *acid plumbifluoride* $3\text{KF} \cdot \text{HF} \cdot \text{PbF}_4$, and is obtained, in 62 p.c. yield, by the action of hydrofluoric acid, of 96 p.c. strength, on lead peroxide. The solution is readily hydrolysed, but this change is prevented by the addition of a soluble fluoride.³⁾ The above acid plumbifluoride is obtained by the action of hydrofluoric acid and potassium fluoride on lead tetracetate, or by fusing equal weights of lead peroxide and potassium hydrogen fluoride⁴⁾, or by adding potassium plumbate to hydrofluoric acid until lead peroxide separates.⁵⁾ It can be crystallised from hydrofluoric acid. When heated in the dry state to 250° , hydrogen fluoride is liberated: at a still higher temperature,

1 W. Biltz, *Ber.*, 1907, **40**, 2182.

2 A. N. Meldrun, *Proc. Chem. Soc.*, 1908, **24**, 340.

3 F. C. Mathers, *Journ. Amer. Chem. Soc.*, 1920, **42**, 1309.

4 Mathers, *op. cit.*

5 G. L. Clark, *Journ. Amer. Chem. Soc.*, 1919, **41**, 1477; see also Brauner, *Journ. Chem. Soc.*, 1894, 393.

fluorine is evolved. Sodium plumbifluoride $2\text{NaK} \cdot \text{PbF}_4$, is prepared by the action of sodium plumbate on hydrofluoric acid; it can be recrystallised from the acid and, when heated to 250° , yields fluorine.

LEAD AND SULPHUR

The *monosulphide*, PbS , has already been described in detail. There is no certain evidence of the existence of a subsulphide.

The *polysulphide*, PbS_n , is a purple-red, unstable compound, produced by the precipitation of ice-cold lead nitrate solution with calcium pentasulphide. Free sulphur is removed by washing the precipitate with carbon disulphide.¹⁾

Lead sub-sulphate is a dark grey substance decomposed by water, prepared by heating lead sub-oxide in methyl sulphate vapour at 280° .²⁾

Lead sulphate is found native as *lead vitriol* or *anglesite*, in transparent rhombic crystals, isomorphous with *celestine* and *heavy spar*. It may be obtained as a white powder by precipitating a lead salt with sulphuric acid, or with a soluble sulphate, or by the action of sulphur dioxide on lead peroxide.³⁾ It may also be obtained crystalline.⁴⁾ Lead sulphate exists in two forms, the transition-temperature of which is 864° . At a temperature slightly higher than this, it loses sulphur trioxide slowly and is estimated to melt at 1170° , forming a white enamel containing basic sulphate. It is easily fusible when mixed with litharge and many salts, such as sodium chloride, sodium sulphate, calcium fluoride and lead chloride. Its solubility in water, determined from its electrical conductivity, by Kohlrausch, is 0.041 gram per litre at 18° ; this is decreased by the addition of alcohol or dilute sulphuric acid.⁵⁾ In concentrated and hot sulphuric acid it is easily

1 Bodroux, *Compt. rend.*, 1900, **130**, 1397.

2 Denham, *Journ. Chem. Soc.*, **114**, 1919, 109.

3 Marino, *Zeitsch. anorg. Chem.* 1907, **56**, 233.

4 Manroß, *Annalen*, 1852, **82**, 360.

5 Sehnal, *Compt. rend.*, 1909, **148**, 1394; Dolezalek and Finckh, *Zeitschr. Anorg. Chem.*, 1906, **51**, 520.

soluble, forming an acid sulphate, and therefore in concentrating sulphuric acid in lead pans, the evaporation must be stopped when the acid has reached about 80 p.c. strength. It is also readily soluble in concentrated hydrochloric acid, in caustic soda solution and in the alkali and ammonium salts of certain acids. In ammonium acetate, up to 3 N strength, lead sulphate is the solid phase; at higher concentrations, the double sulphate $(\text{NH}_4)_2\text{SO}_4 \cdot \text{PbSO}_4$ is in equilibrium with the saturated solution.¹⁾ Some data connecting solubility and concentration of the ammonium salt are given herewith:²⁾

| | Temp. = 25° | | | Temp. = 100° | | | |
|--|-------------|-------|-------|--------------|------|-------|-------|
| Grams Ammonium Acetate per litre | 7.98 | 15.06 | 31.92 | 280 | 320 | 370 | 450 |
| Grams Lead Sulphate per litre | 0.636 | 1.38 | 3.02 | 71.2 | 98.8 | 105.8 | 111.0 |

In solution of sodium acetate, the solid phase is lead sulphate, and in potassium acetate, the double sulphate $\text{K}_2\text{SO}_4 \cdot \text{PbSO}_4$ according to Fox (*op. cit.*). Ammonium tartrate, calcium acetate and many other salts similarly increase the solubility of lead sulphate.³⁾ A double sulphate of lead and tin, $\text{PbSO}_4 \cdot \text{Sn}(\text{SO}_4)_2$ is formed by mixing sulphuric acid solutions of lead sulphate and orthostannic acid.⁴⁾

The reduction of lead sulphate by means of lead, carbon and carbon monoxide has already been noted, as well as the technically-important decomposition of the salt with silica. Upon the formation of lead silicate in the last reaction depended the use of lead sulphate as a glaze (*alquifoux*) in the pottery industry. Stas found that lead sulphate could not be completely dried in glass vessels without attacking the glass.

1 J. J. Fox, *Proc. Chem. Soc.*, 1909, **25**, 355.

2 Noyes and Whitcomb, *Journ. Amer. Chem. Soc.*, 1905, **27**, 756; Dunnington and Long, *Amer. Chem. Journ.*, 1899, **22**, 217.

3 Long, *Amer. Chem. Journ.*, **22**, 217; Reichard, *Chem. Zeit.*, 1903, **27**, 924. 943.

4 R. F. Weinlund and H. Kühn, *Ber.*, 1906, **39**, 2751.

Two reversible reactions which lead sulphate undergoes are of interest. The first, represented by the equation:¹⁾



indicates a possible method of conversion of anglesite into cerussite, and the reverse, under natural conditions. The second reaction is between lead sulphate and potassium iodide



This reaction exhibits a thermal change of sign at 8°.²⁾

Lead disulphate or *Plumbic sulphate* $\text{Pb}(\text{SO}_4)_2$ is obtained at the anode when pure sulphuric acid, of sp.gr. 1.7—1.8 is electrolysed between lead electrodes. It is a white, or faintly greenish-yellow, crystalline powder, giving a green solution in concentrated sulphuric acid. It is decomposed by water, forming sulphuric acid and lead peroxide, and is a powerful oxidising agent. It forms double salts with the alkali metals and also with aniline and with dimethyl and diethyl aniline.³⁾

Lead Sulphite, PbSO_3 , is prepared by precipitation of an alkali sulphite solution with a lead salt: it is converted by oxidising agents into lead sulphate. It does not appear to be formed by the direct action of sulphur dioxide on lead oxide.

Lead Thiosulphate, PbS_2O_3 , is precipitated from dilute solutions of lead salts by the addition of excess of sodium thiosulphate, but a concentrated solution of sodium thiosulphate, treated with excess of a saturated solution of lead chloride, yields the compound $\text{PbCl}_2 \cdot 2\text{PbS}_2\text{O}_3$. On warming, the white lead thiosulphate turns black, owing to the formation of lead sulphide; lead sulphate, sulphur and sulphuric acid are also produced during the decomposition.⁴⁾

Lead selenide and *Lead telluride* occur naturally as the rare minerals clausenthalite and altaite, corresponding to galena in composition and they can be synthesised from their con-

1 Strömholm, *Zeitschr. anorg. Chem.*, 1904, **38**, 443.

2 Klein, *Zeitschr. Phys. Chem.*, 1901, **36**, 360.

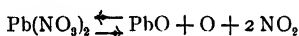
3 Elbs and Fischer, *Zeitsch. Electrochem.*, 1900, **7**, 343.

4 W. H. Perkins and A. T. King, *Proc. Chem. Soc.*, 1912, **28**, 407.

stituents. Selenites, selenates, tellurites and tellurates of lead resemble the corresponding sulphur compounds.

LEAD AND NITROGEN

Lead nitrate $\text{Pb}(\text{NO}_3)_2$ is formed by dissolving litharge in nitric acid of sp.gr. 1.35. The solution is evaporated until it has the sp.gr. 1.6, and is then allowed to cool. It forms milk white crystals from water, clear crystals from nitric acid, of sp.gr. 4.5 and dissolves in water with a reduction of temperature. It has an astringent metallic taste, detonates with brilliant sparks when thrown upon red-hot charcoal and deflagrates when triturated with sulphur. When heated it begins to decompose at 283° , and in an evacuated and sealed tube it dissociates thus:



The dissociation-pressure is a function of the temperature; the data illustrating this relationship are:¹)

| | | | | | | | |
|--------------------------------------|-----|-----|------|------|------|-------|--------|
| Temperature $^\circ\text{C}$ | 223 | 230 | 250 | 274 | 296 | 357 | 448 |
| Pressure (mm mercury) | 6.2 | 6.9 | 11.8 | 32.6 | 78.4 | 514.0 | 1180.0 |

Stas found that perfectly dry lead nitrate can be heated to 300° without decomposition. The drying of the salt requires 8—12 days' continuous heating at 140 — 155° , in a current of dry air. If, in the preparation of the nitrate from lead and nitric acid, the action of the acid be not continuous, then the salt loses weight steadily during the drying process. Lead nitrate is used in dyeing and calico printing, for the preparation of mordants and of chrome yellow.

Lead nitrite $\text{Pb}(\text{NO}_2)_2$ is obtained by the interaction of silver nitrite and lead chloride; after filtering, the solution is concentrated in a vacuum. It forms yellow prisms, soluble

Baekeland, *Journ. Amer. Chem. Soc.* 1904, **26**, 391; Morgan, *Journ. Phys. Chem.* 1904, **8**, 416; Colson, *Compt. rend.* 1909, **148**, 837.

in water, the solution on evaporation losing nitric oxide and yielding a basic nitrite.¹⁾

Lead hyponitrite $\text{Pb}(\text{NO})_2$ is a yellow crystalline powder, which explodes on heating.²⁾ It is prepared by precipitating lead acetate solution with sodium hyponitrite.

Lead nitrohydroxylamine PbN_2O_3 is an unstable salt.³⁾

Lead imide PbNH is obtained by the action of potassamide on lead iodide in liquid ammonia. It is a reddish-brown explosive substance. If the lead iodide be in excess, a white compound $\text{NPb}_2\text{I} \cdot \text{NH}_3$ is formed.⁴⁾

Lead nitride, or *azide*, PbN_6 , is formed by the action of an alkali azoimide on lead salts.⁵⁾ It is sensitive to light like the azides of silver and mercury.⁶⁾ A nitride of lead is also produced by the electrical dispersal of lead in liquid nitrogen. It is explosive; it has not been obtained pure and it is not known whether it is identical with the above azide.⁷⁾

Lead Cyanide is precipitated by the addition of hydrocyanic acid, or potassium cyanide solution, to a lead salt, either as the normal or the basic salt, according to conditions. If the precipitate be boiled with 5 p.c. hydrocyanic acid, the normal cyanide, $\text{Pb}(\text{CN})_2$, crystallises on cooling. The compound is readily hydrolysed.⁸⁾

Lead Cyanate, $\text{Pb}(\text{CNO})_2$, is prepared by the usual methods and is very readily hydrolysed, yielding thereby urea.⁹⁾

The *ferricyanides* with the formulae $\text{Pb}_3[\text{Fe}(\text{CN})_6]_2 \cdot 16\text{H}_2\text{O}$ and $\text{K}_2\text{Pb}_2[\text{Fe}(\text{CN})_6]_2 \cdot 3\text{H}_2\text{O}$, alleged to be produced by the

1 Chilesotti, *Atti, R. Accad. Lincei*, 1908, [v], 17, [i], 173, 288, 377; 474, 824; Meldrum, *Chem. Soc. Proc.* 1908, 97.

2 Kirschener, *Zeitsch. anorg. Chem.* 18, 424; Divers, *Chem. Soc. Trans.* 1899, 121.

3 Angelico and Fanara, *Gazz. chim. ital.* 31, [ii] 15.

4 Franklin, *Journ. Amer. Chem. Soc.* 1905, 27, 820.

5 Curtius and Rissom, *Journ. pr. Chem.* [ii], 58, 261.

6 L. Wöhler and W. Krupto, *Ber.*, 1913, 46, 2045.

7 F. Fischer and F. Schröter, *Ber.*, 1910, 43, 1442, 1454, 1465.

8 N. M. Gupta, *Proc. Chem. Soc.*, 1913, 29, 421.

9 A. C. Cumming, *Proc. Chem. Soc.*, 1903, 19, 272.

action of potassium ferricyanide on lead acetate, are stated not to exist. The compound formed in this reaction is $\text{Pb}_3[\text{Fe}(\text{CN})_6]\text{NO}_3 \cdot 5\text{H}_2\text{O}$.¹⁾

LEAD AND PHOSPHORUS

Tribasic lead phosphate $\text{Pb}_3(\text{PO}_4)_2$ is an amorphous white powder, obtained by precipitating an excess of lead acetate with a small quantity of sodium phosphate at 100° , or by boiling the dibasic salt in water for 5–6 hours.

Dibasic lead phosphate PbHPO_4 is prepared by precipitating a somewhat dilute solution of lead nitrate with hot dilute phosphoric acid at 100° . It forms a fine crystalline powder.

Monobasic lead phosphate $\text{Pb}(\text{H}_2\text{PO}_4)_2$ is formed by dissolving the dibasic salt in hot concentrated phosphoric acid and allowing the solution to crystallise. It may then be recrystallised from phosphoric acid. It forms fine needles stable in air, and is decomposed by cold and still more readily by boiling water, forming first the dibasic and finally the tribasic salt.²⁾

Lead pyrophosphates, a number of complex phosphates and *thiophosphates*³⁾, and also *lead phosphites*⁴⁾, have been prepared.

LEAD AND ARSENIC

Lead arsenate may be formed by suspending litharge in a solution of arsenic acid, in the presence of nitric or acetic acid as catalyst⁵⁾ or by roasting a mixture of white arsenic

1 E. Müller and O. Diefenthaler, *Ber.*, 1910, **43**, 2321.

2 Alders and Stähler, *Ber.*, 1909, **42**, 2261.

3 Gerhardt, *Ann. Chim. Phys.*, 1848, [III], **22**, 505; Ouvrard, *Compt. rend.* 1890, **110**, 1334; Friedel, *ibid.* 1894, **119**, 260; Ferrand, *ibid.* 1896, **122**, 886.

4 Amat, *ibid.* 1890, **110**, 901.

5 U.S. Pats. 892603, 903389, 1908; *Journ. Soc. Chem. Ind.* 1908, 1019, 1203.

and a lead salt in equivalent proportions, in the presence of oxygen or an oxidising agent.¹⁾

Lead arsenate is used as an insecticide and is largely employed in the United States for the protection of fruit trees from the larvae of the gypsy moth. For this purpose, it is said to be best prepared by adding a solution of lead acetate or nitrate to sodium arsenate, until an iodine test paper shows the presence of excess of lead.²⁾ The precipitate is a mixture of basic arsenate $Pb_3OH(AsO_4)_3$ and dibasic lead arsenate, $PbHAsO_4$.³⁾ For spraying plants, it is often mixed with lime-sulphur solution; in this case, the normal lead salt should be employed, and it is best to avoid using water containing much alkali carbonate, as the tendency of the latter is to make the arsenic soluble.⁴⁾ When used as a spray in viniculture, arsenic is present in the grapes as harvested, but not in the wine.

LEAD AND ANTIMONY

Lead Antimonate is formed as an oily liquid during the softening of hard lead, and results also from the interaction of solutions of antimonie acid and lead acetate, the latter method yielding a hydrate of the compound $Pb(SbO_3)_2$. It is also a constituent of the pigment known as Naples Yellow, which is prepared by heating either 2 parts by weight of red lead and 1 part of potassium pyroantimonate, or a mixture of 1 part of potassium antimonyl tartrate (tartar emetic), 2 of lead nitrate and 4 of sodium chloride.

LEAD AND BISMUTH

From the thermal study of systems composed of lead monoxide (m.p. 870°) and bismuth trioxide (m.p. 817°), the

1 U.S. Pat. 929962, 1909.

2 Haywood and M'Donnell, *Journ. Soc. Chem. Ind.* 1910, 1027; see also Pickering, *Journ. Chem. Soc.* 1907, 312.

3 *Journ. Amer. Chem. Soc.* 1916, 38, 2027.

4 Brady and Tartar, *Journ. Ind. Eng. Chem.* 1910, 2, 328; see also Griffen, *ibid.* 1909, 1, 659; Moréau and Vinet, *Compt. rend.* 1910, 150, 787.

existence of the following compounds has been inferred:
 $\text{PbO} \cdot 4\text{Bi}_2\text{O}_3$ (m.p. 695°); $2\text{PbO} \cdot 3\text{Bi}_2\text{O}_3$ (m.p. 686°) and
 $2\text{PbO} \cdot \text{Bi}_2\text{O}_3$ (m.p. 625°).¹⁾

LEAD AND SILICON

The chief natural and artificial silicates of lead, as well as lead silicofluoride, have already been considered. Silicates of lead enter into the composition of optical glasses, Flint Glass, for example, containing $\text{PbO} = 44$, $\text{K}_2\text{O} = 12$, $\text{SiO}_2 = 44$ p.c. Such glass is not suitable for chemical work, owing to the ease with which it is attacked by hydrochloric acid. Lead glass containing 50 p.c. of lead oxide, and 50 p.c. of silica is not dulled by hydrogen sulphide, whereas the same glass fused with potash in the proportions of 8 to 1 is rendered dull by this gas.²⁾ The molecular ratio of acidic to basic oxides in this pure lead glass is 3.7, in the lead potash glass derived from it, 2. It has been found by Thorpe and Simmonds, that the solubility of lead silicates in hydrochloric acid is similarly dependent on this molecular ratio of acidic to basic oxides: when the ratio is less than 2:1, then the silicate is easily attacked by dilute hydrochloric acid, the lead passing into solution, and when the ratio is greater than this, there is little or no action. Addition of soda to the silicate, increases the solubility of the lead, but alumina has the reverse effect.³⁾ These facts have an important bearing on the use of lead frits in the pottery trade, since the hygienic advantage of replacing "raw lead" (i.e. lead monoxide, red lead or white lead) by silicate frits would be partly neutralised if the lead in the frits were easily soluble in the weak acid of the gastric juice.

LEAD AND BORON

Lead Borates are prepared by precipitation of lead salts with borax solution. According to conditions, the metaborate $\text{Pb}(\text{BO}_2)_2 \cdot \text{H}_2\text{O}$, or polyborates of the type $\text{PbO} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$.

¹ C. Belladen, *Gazz. chim. ital.* 1922, 52, [11], 160.

² Faraday, *Phil. Trans.*, 1830, 1.

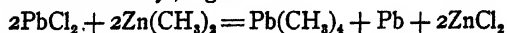
³ Sir E. Thorpe and C. Simmonds, *Journ. Chem. Soc.* 1901, 79, 794; 1910, 97, 2282.

are produced. Litharge and boric oxide yield a glass when fused together: one definite compound has been isolated from the melt, viz. $\text{PbO} \cdot 3\text{B}_2\text{O}_3$.¹⁾ When the ratio is $\text{PbO} : 3\text{B}_2\text{O}_3$, a uniform glass is obtained, but with excess of boric oxide over this ratio, the melt separates into two layers, the upper of which consists of boric oxide. Mixtures containing more lead than corresponds to the ratio $2\text{PbO} : \text{B}_2\text{O}_3$ yield glasses which devitrify even on rapid cooling.²⁾ Faraday's famous borate glass was made by fusing 112 parts by weight of litharge with 72 of boric oxide.

LEAD AND CARBON

Lead, like all the metals of the odd series of the long periods in the periodic classification, does not form a carbide, though it presumably unites directly with the carbon of hydrocarbon radicles in the organo-metallic compounds. The typical derivatives of this class are those containing quadrivalent lead, and the tendency of the lead to assume the higher valency is so pronounced that when plumbous salts are used in their preparation, metallic lead is separated; lead itself (alloyed with sodium) is easily and directly converted into the tetra-alkyl derivatives. Within recent years, organo-metallic derivatives, of trivalent lead, and, of bivalent lead also have been isolated. They are unsaturated and the metal they contain tends to pass to the higher stage of oxidation.

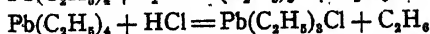
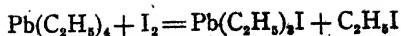
The lead tetra-alkyl compounds are prepared by the action of alkyl iodides on lead-sodium alloy, or from lead, chloride and zinc alkyl, e.g.:—



These alkyl compounds are colourless liquids, not soluble in water, or attacked by it. They react with hydrochloric acid yielding a tri-alkyl chloride and with iodine to form a tri-alkyl iodide, thus:—

1 Le Chatelier, *Bull. Soc. Chim.*, 1899 [III], 21, 35; H. V. Thompson, *Trans. Eng. Ceram. Soc.*, 1918—19, 18, 510.

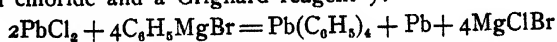
2 Le Chatelier, *La Silice et les Silicates*; 1914, p. 242.



These products are salts of a base, plumbonium hydroxide, $\text{Pb}(\text{C}_2\text{H}_5)_3\text{OH}$ and they yield this by reaction with silver oxide, or distillation with caustic alkali. The base itself is crystalline, strongly alkaline, has a smell of mustard, and yields on neutralisation with acids the corresponding salts; of these the sulphate is sparingly soluble:

Lead tetramethide, $\text{Pb}(\text{CH}_3)_4$, boils at 110° and has sp.gr. 2.034; it is of particular interest in that it is volatile without decomposition; its vapour density at 130° is 9.52 (air = 1), in close agreement with the calculated value, 9.25.

Lead tetraphenyl $\text{Pb}(\text{C}_6\text{H}_5)_4$ is made either by the interaction of phenyl bromide and sodium-lead alloy¹), or from lead chloride and a Grignard reagent²):



It crystallises in colourless needles, tetragonal in form, melts at $224-5^\circ$ and is decomposed in the neighbourhood of 300° . The reactions of this compound with chlorine, nitric acid and acetic acid, whereby the compounds $\text{Pb}(\text{C}_6\text{H}_5)_2\text{Cl}_2$, $\text{Pb}(\text{C}_6\text{H}_5)_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Pb}(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ are produced are of importance, since these derivatives are salts of a base (unknown) $\text{Pb}(\text{C}_6\text{H}_5)_2(\text{OH})_2$, or its anhydride, $\text{Pb}(\text{C}_6\text{H}_5)_2\text{O}$. This base thus bears the same relation to plumbonium hydroxide as the sulphoxides due to sulphonium hydroxide, and its basic properties are as well, or better, developed as are those of the sulphoxides.³)

At a low temperature, bromine reacts with lead tetraphenyl to form the triphenyl bromide, $\text{Pb}(\text{C}_6\text{H}_5)_3\text{Br}$, m.p. 166° , which by double decomposition with an alkali iodide yields the iodide, $\text{Pb}(\text{C}_6\text{H}_5)_3\text{I}$ m.p. 142° . From the latter, the base $\text{Pb}(\text{C}_6\text{H}_5)_3\text{OH}$ can be prepared by the agency of caustic alkali

¹ Polis, *Ber.*, 1887, 20, 717, 3332.

² P. Pfeiffer and P. Truskier, *Ber.*, 1904, 37, 1125.

³ J. Hermann, *Ber.*, 1905, 38, 2824; 1906, 39, 3812; J. Tafel, *Ber.*, 1911, 44, 323; E. Fromm, *Ann.*, 1913, 396, 75.

and from this base the colourless chloride, $\text{Pb}(\text{C}_6\text{H}_9)_3\text{Cl}$ m.p. 206° . Hydrogen sulphide reacts with the chloride, yielding a white precipitate of the sulphide, $[\text{Pb}(\text{C}_6\text{H}_9)_3]_2\text{S}$.¹)

Lead tricyclohexyl $\text{Pb}(\text{C}_6\text{H}_{11})_3$ is prepared by the addition of lead chloride to a solution of magnesium cyclohexyl bromide in dry ether. It forms yellow, hexagonal plates, decomposing at 195° , and combines with iodine at the ordinary temperature to form the iodide $\text{Pb}(\text{C}_6\text{H}_{11})_3\text{I}$, from which the hydroxide and other compounds can be prepared by the usual methods. The molecular weight, determined cryoscopically, agrees with the formula given above, so that the triaryl may be regarded as containing tervalent lead, and thus analogous to Gomberg's triphenylmethyl.²)

Other compounds, containing tervalent lead, have been isolated by similar methods, e.g. the tri-o-tolyl, tri-p-tolyl and the tri-xyllyl compound.³)

By the electrolysis of sulphuric acid, containing acetone, $\text{C}_3\text{H}_8\text{O}$, with lead electrodes, a red oil, highly unsaturated in character, is obtained. This probably contains lead di-isopropyl, $\text{Pb}(\text{C}_3\text{H}_7)_2$. It absorbs oxygen from the air, yielding lead peroxide and a strongly basic compound, probably $\text{Pb}(\text{C}_3\text{H}_7)_2\text{O}$, analogous in composition and basicity to the sulphoxides (*v. supra*), which when dissolved in acetic acid and treated with potassium bromide furnishes the crystalline lead dialkyl bromide, $\text{Pb}(\text{C}_3\text{H}_7)_2\text{Br}_2$. The bromide is also produced on brominating the red oil; it is converted into the nitrate with silver nitrate, and from this the chloride, $\text{Pb}(\text{C}_3\text{H}_7)_2\text{Cl}_2$ is precipitated with an alkali chloride. Similarly, from the nitrate solution, the bromide, iodide, sulphate, chromate and sulphide (white at first, turning black owing to conversion into lead sulphide) can be precipitated. The unsaturated dialkyl $\text{Pb}(\text{C}_3\text{H}_7)_2$ thus behaves, analytically, like lead itself, in the plumbous salts.⁴)

1 G. Grüttner and Gertrud Grüttner, *Ber.*, 1918, **51**, 1293; 1298.

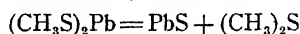
2 E. Krauss, *Ber.*, 1921, **54**, [B], 2060.

3 E. Krauss and G. G. Reißaus, *Ber.*, 1922, **55**, [B], 888.

4 J. Tafel, *Ber.*, 1911, **44**, 323.

Lead ethoxide $\text{Pb}(\text{OEt})_2$ has been prepared by suspending thin sheets of lead over absolute alcohol, through which a stream of ozone is passed. When washed with alcohol and dried *in vacuô* over sulphuric acid, it forms a light yellow friable powder, soluble in water, but readily hydrolysed by it.¹⁾

Mercaptans are precipitated by alcoholic solutions of lead acetate, and the resulting lead mercaptides are decomposed by hydrochloric acid, with formation of lead chloride and regeneration of the mercaptan. The mercaptides on heating yield the organic monosulphides, thus ²⁾:



The lead salts of organic acids are usually insoluble in water and, as the regeneration of the acid is readily accomplished by the agency of hydrogen sulphide, they are largely used in organic chemistry, in order to separate acids from impure liquors and to obtain them in a state of purity. The lead salts of some of the fatty acids are easily soluble in water, e.g. the formate, acetate and propionate. The solution of the propionate is distinguished from the formate and acetate by the deposition of an insoluble basic salt on boiling. The glycolate shows a similar behaviour; the acrylate of lead is the best characterised salt of acrylic acid. Lead oleate is soluble in ether and this property is of value in the separation of oleic acid from palmitic and stearic acids, which are so often associated with it, since the lead salts of the last two are insoluble in ether.

Lead acetate crystallises well in the form of the hydrate; $\text{Pb}(\text{C}_2\text{H}_3\text{O})_2 \cdot 3\text{H}_2\text{O}$, which crystallises in the monoclinic system and loses water of crystallisation at 100° , or when preserved in a desiccator over sulphuric acid: the hydrated salt melts at 75° , the anhydrous salt at 280° . On heating above this point, decomposition occurs, with production of acetic acid, acetone, carbon dioxide and metallic (pyrophoric) lead. It is very soluble in water, 1 part by weight of the salt dissolving in

¹ F. M. Perkin, *Chem. Soc. Proc.*, 1908, 179.

² Klason, *Ber.*, 1887, 20, 3412.

1.5 of water at 15°, in 1 at 40°, and 0.5 at 100°: it is also fairly soluble in alcohol, 100 grams of the latter dissolving 3.3 grams at 25° and its own weight of the salt at 100°.

Lead tetra-acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$, is produced either by the oxidation of the diacetate with chlorine, or by dissolving red lead in warm acetic acid. It separates from acetic acid solutions in white needles, melting at 175°, it is decomposed by water yielding lead peroxide, and hydrochloric acid converts it into the tetrachloride of lead. It is one of the most stable of the salts of lead of this type. Similar salts have been prepared from other fatty acids.¹⁾

The lead salts of the acids derived from the metals of the titanium and the vanadium groups, and from manganese (manganic and permanganic acids) do not appear to have been closely examined. Two naturally-occurring vanadates are decloizite, $\text{Pb}_2\text{V}_2\text{O}_7$, and mottramite, a basic orthovanadate of lead and copper. In the chromium group, there are three salts of lead which occur native as the minerals crocoite PbCrO_4 ; wulfenite, PbMoO_4 ; and stolzite, PbWO_4 , the last two of which have been prepared synthetically, by fusing the sodium salt of the acid in question with lead chloride. The lead molybdate melts at 1065°, the tungstate at 1123°. The remaining metal of this group, also forms a lead derivative namely, that of diuranic acid, $\text{PbO} \cdot 2\text{UO}_3$. The chromates of lead deserve further consideration owing to their extensive use as pigments.

Lead Chromate, PbCrO_4 , is precipitated from acetic acid solutions of lead salts, by the addition of a soluble chromate as a heavy yellow precipitate, sp.gr. 5.6, practically insoluble in water, but soluble in caustic soda and in dilute hydrochloric and nitric acids. It is trimorphous, one form being stable below 707°, another from 707° to 783°, and the third form from 783° to its melting point, 844°. On a large scale, litharg is dissolved either in acetic acid or nitric acid and the dilute solution of the salt is run into dilute solution of sodium o

¹ Hutchinson and Pollard, *Journ. Chem. Soc.*, 1896, 60, 202.

potassium dichromate, under constant stirring, and at the ordinary temperature. Lighter shades are obtained by the co-precipitation of lead sulphate from sodium sulphate and the presence of 10 p.c. of this has the effect of preventing the yellow chromate of lead becoming orange and losing its lustre¹); they are also produced by carrying out the precipitation in liquors containing suspended barium sulphate. The pigment comes into the market under various names, e.g. chrome yellow, Paris yellow, canary yellow. It is also used in calico-printing, being either precipitated directly on the fabric; or used in the form of a fine suspension in water.

Basic chromates are also used as pigments under the names of chrome orange, chrome red, chinese red, Derby red, etc. They are prepared by heating precipitated chrome yellow, after decanting the liquor, with caustic soda or milk of lime. The red forms become orange on trituration.

The existence of lead dichromate $\text{PbO} \cdot 2\text{CrO}_3$ has been denied²), but it was prepared by Meyer³) in the form of a reddish-brown crystalline meal, by heating for several hours a mixture of lead acetate, chromic anhydride and sulphuric acid ($D = 1.4$). It is also formed, along with an equal amount of the monochromate, by boiling lead acetate with chromic acid.

LEAD SALTS WITH DIFFERENT ACID RADICLES

Lead salts with different acid radicles are not uncommon. Many of these are well characterised and occur naturally and the greater number of them contain a halide, usually a chloride.

Two well-defined minerals are phosgenite or cromfordite, the chloro-carbonate, $\text{PbCl}_2 \cdot \text{PbCO}_3$, and leadhillite, the basic sulphato-carbonate $\text{PbSO}_4 \cdot 2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$. Several chloro-sulphides have been described. $\text{PbS} \cdot \text{PbCl}_2$ is the brown precipitate formed by the action of hydrogen sulphide on lead

¹ C. Zablczyński, *Chem. Ind.*, 1908, **31**, 731.

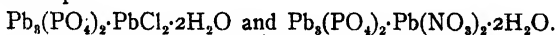
² W. Authenrieth, *Ber.*, 1902, **35**, 2057.

³ Otto Meyer, *Ber.*, 1903, **36**, 1740.

chloride, in the presence of fairly concentrated hydrochloric acid.¹⁾ The reddish-brown precipitate, produced by pouring a cold solution of galena in concentrated hydrochloric acid into water, is said to be $\text{PbS} \cdot 4\text{PbCl}_2$. Similar derivatives of bromide and iodide of lead have also been described. These compounds may be regarded as the sulphur analogues of the basic chlorides, $\text{PbS} \cdot \text{PbCl}_2$ for example, corresponding to matlockite.

Solutions of lead halides in sodium thiosulphate are sensitive to light, the chloride depositing red crystals of $\text{Pb}_4\text{S}_4\text{Cl}_2$, and the iodide, a copper-red precipitate of the formula $\text{Pb}_3\text{S}_4\text{I}_2$. Similar compounds are produced by the action of an alkali polysulphide on the aqueous solution of the lead halide and may thus be regarded as chloro- and iodo-disulphides; oxygen analogues to these are unknown.²⁾

The group of minerals, isomorphous with apatite, all contain the elements of lead chloride (or fluoride) along with those of a lead salt of the phosphorus group, the chief members being pyromorphite $3\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbCl}_2$; mimetite; $3\text{Pb}_3(\text{AsO}_4)_2 \cdot \text{PbCl}_2$ and vanadinite $3\text{Pb}_3(\text{VO}_4)_2 \cdot \text{PbCl}_2$; Camphylite is the isomorphous mixture of the chloro-phosphate and chloro-arsenate. Somewhat similar salts have been prepared by precipitation of alkali phosphate solutions with lead salts, for example:



The double salt $\text{Pb}(\text{NO}_3)_2 \cdot \text{Pb}(\text{H}_2\text{PO}_2)_2$ prepared from solutions of lead nitrate and lead hypophosphite is explosive; its use in percussion caps has been recommended.³⁾ A phosphato-uranate of lead occurs naturally as the mineral dewindtite $4\text{PbO} \cdot 3\text{P}_2\text{O}_5 \cdot 8\text{UO}_3 \cdot 12\text{H}_2\text{O}$.

The simple chlor-acetate, $\text{PbCl}_2 \cdot \text{PbAc}_2$, was prepared by Carius.⁴⁾ Many similar compounds have been prepared, of

1 Parmentier, *Compt. rend.*, 1892, **114**, 299.

2 K. A. Hofmann and V. Wölfl, *Ber.*, 1905, **38**, 349.

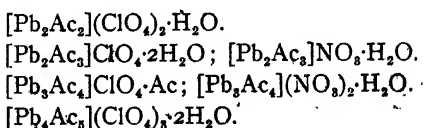
3 E. von Herz, *Zeits. des Schieß- u. Sprengstoffw.*, 1916, **11**, 365, 388.

4 *Ann.*, 1863, **125**, 87. The symbol Ac denotes the acetate radicle, $\text{C}_2\text{H}_3\text{O}_2$.

which the following may serve as examples: $\text{PbCl}_2 \cdot \text{PbAc}_2 \cdot 2\text{HAc}$; $\text{PbI}_2 \cdot \text{PbAc}_2 \cdot 2\text{KAc}$.

By warming litharge with a mixture of perchloric and acetic acids, and by the action of nitric acid on lead acetate solutions; aceto-perchlorates and aceto-nitrates of lead are formed, many of which are well crystallised and some of which can be recrystallised from pure water without change. Thus the compound $\text{PbAc}_2 \cdot \text{Pb}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ is obtained from litharge (44.6 gram), perchloric acid (44.4 c.c. of 50 p.c. acid) and acetic acid (5.9 grams), and the compound, $2\text{PbAc}_2 \cdot \text{Pb}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ by the action of 2.8 grams of nitric acid on a solution of 22.8 grams of lead acetate in 10 c.c. of water. As measurements of electrical conductivity show that the first of these salts yields three ions in solution, it may be represented by the symbol $[\text{Pb}_2\text{Ac}_2](\text{ClO}_4)_2$, the complex in square brackets denoting the cation, whilst the chlorate radicle furnishes the anion. A more extreme case is that of the salt $5\text{PbAc}_2 \cdot 3\text{Pb}(\text{ClO}_4)_2$, the solution of which behaves as a four-ion salt and is thus written $[\text{Pb}_4\text{Ac}_5](\text{ClO}_4)_3$.

The formulae of the complex salts prepared, symbolised in this manner¹, are:



BASIC SALTS OF LEAD

The basic salts of lead have been studied by many different methods. The moderate basicity of the metal is evidenced by the hydrolysis which its normal salts undergo when greatly diluted, particularly when the temperature is raised to the boiling point. The reversible reaction of hydrolysis, represented by the equation:



R. Weinland and R. Stroh, *Ber.*, 1922, 55, 2219.

may lead in extreme cases to precipitation of the hydrated oxide, as indicated; more usually, reaction between normal salt and hydroxide occurs, with formation of basic salts, which, in general, will increase in basicity with increasing dilution.

Addition of alkali to solution of normal salt, has the same effect as dilution, since it lowers the concentration of the acid, HX ; otherwise regarded, it affords opportunity for the production of lead hydroxide from lead ions and hydroxyl ions and subsequent reaction between lead hydroxide and normal salt results in the formation of basic salt.

The method largely used by Strömholm¹) is, in a sense, the reverse of these. A suspension of lead hydroxide is shaken with a solution of alkali salt (0.05 normal) until the hydroxyl concentration of the liquor is constant. Opportunity is thus afforded for the production of the normal salt, which by its union with unaltered hydroxide of lead, yields the basic salt.

These methods are of service in the preparation of sparingly soluble basic salts, but they suffer naturally from the poor characterisation of the products, which frequently rest under the suspicion of being heterogenous. They throw light, nevertheless, on the processes which have been operative under natural conditions in the formation of minerals of basic composition, many of which are splendidly crystallised, despite their insolubility. In many cases, already discussed, where these minerals have been formed from lead, or lead slags, by the agency of sea water, or by ordinary weathering, the data are available for estimating the time required to produce in crystalline form what, under laboratory conditions, can only be obtained as a granular, and possibly amorphous powder. Many of the basic salts of lead are readily soluble in hot water and can be got in a crystalline condition from their solutions. Such salts, like the basic nitrate, are easily prepared by dissolving oxide of lead in the normal salt solution. The basic chlorates, recently investigated, are especially distinguished by their ready solubility, ease of preparation and of crystallisation, and ability to enter into reactions of

¹ D. Strömholm, *Zeit. anorg. Chem.*, 1904, **38**, 429.

double decomposition.¹⁾ These will be considered in detail later. Such methods, in which aqueous solutions are utilised, frequently yield hydrated basic salts.

The study of fused mixtures of lead oxide and lead salts, by the methods of thermal analysis, has furnished much information concerning the equilibria in such systems, and has led to the characterisation of many (anhydrous) basic salts. The chief basic salts examined in this way are the chlorides²⁾, sulphates³⁾, chromates, molybdates and tungstates.⁴⁾

Basic Halides. The following are known, the order being that of increasing basicity.

1. $\text{PbO} \cdot 2\text{PbCl}_2$ occurs as the mineral penfieldite.
2. $\text{PbO} \cdot \text{PbCl}_2$ is the mineral matlockite. It exists, according to Ruer, in melts of litharge and lead chloride, is decomposed at 524° into the next more basic chloride and lead chloride. The hydrate $\text{PbO} \cdot \text{PbCl}_2 \cdot \text{H}_2\text{O}$ or $\text{Pb}(\text{OH})\text{Cl}$ occurs as the mineral laurionite and was once prepared on a large scale by the precipitation of lead chloride solution with milk of lime, being known as Pattinson's White.
3. $2\text{PbO} \cdot \text{PbCl}_2$ is the mineral mendipite. The artificial preparation melts at 693° .
4. $3\text{PbO} \cdot \text{PbCl}_2$ is pseudo-mendipite. A hydrate of the composition, $3\text{PbO} \cdot \text{PbCl}_2 \cdot \text{H}_2\text{O}$ was isolated by Strömholm.
5. $4\text{PbO} \cdot \text{PbCl}_2$ melts, according to Ruer, at 711° . The hydrate, $4\text{PbO} \cdot \text{PbCl}_2 \cdot 2\text{H}_2\text{O}$ is produced by shaking litharge with sodium chloride of normal strength.⁵⁾
6. $6\text{PbO} \cdot \text{PbCl}_2 \cdot 2\text{H}_2\text{O}$ was isolated by Strömholm; the anhydrous salt is unknown.
7. $13\text{PbO} \cdot 2\text{PbCl}_2$ is the mineral loretoite.
8. $7\text{PbO} \cdot \text{PbCl}_2$ is the mineral chubutite. The relationships among the minerals of this group are described on p. 34. The pigment known as Cassel's Yellow is supposed to consist

1 R. Weinland and R. Stroh, *Ber.*, 1922, **55**, 2706.

2 Ruer, *Zeitsch. anorg. Chem.*, 1906, **49**, 365.

3 Schenck and Raßbach, *Ber.*, 1908, **41**, 2917.

4 Jaeger and Germs, *Zeitschr. anorg. Chem.*, 1921, **119**, 145.

5 Berl and Austerweil, *Zeit. electrochem.*, 1907, **13**, 165.

argely of this basic chloride. It appears to be produced by heating the hydrate No. 6 above, or the basic salt formed by digesting, for several days, a ground-up paste of litharge and one quarter of its weight of common salt. It is usually prepared by heating to fusion, either 10 parts of litharge by weight and 7 of sal ammoniac, or 10 parts of lead peroxide, red lead or white lead with 1 part of sal ammoniac.

Many basic salts of other acids, similar to the above, were prepared by Strömholm, who found that those conforming to the type $\text{PbO} \cdot \text{PbX}_2$ (No. 2* above) usually crystallise with one mol. of water, though the chromate and sulphate are anhydrous. These of type 4 are particularly common and include, besides the three halides, the bromate, iodate, sulphate, selenate and chromate. Only the nitrate and oxalate could be prepared corresponding to type 3, and the halides and sulphocyanide of type 6. The nitrate of the formula $5\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ exists, though there is no corresponding chloride.

Basic Sulphates. Three of these are known: $2\text{PbO} \cdot \text{SO}_3$ is the mineral lanarkite. It is also prepared by the action of ammonia on lead sulphate, and by fusing lead oxide and lead sulphate; it melts at 977° . $3\text{PbO} \cdot \text{SO}_3$ is dimorphous, having a transition-temperature at 450° , and melting at 961° .

$4\text{PbO} \cdot \text{SO}_3$ is decomposed at 897° into litharge and the tribasic sulphate. (Jaeger and Germs.)

The hydrate salt is formed by the action of ammonium sulphate on lead hydroxide. The pigment known as sublimed white lead, or Purex, is possibly a basic sulphate.

Basic Nitrates. The compound $\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ($\text{Pb}(\text{OH})\text{NO}_3$ or $2\text{PbO} \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$) is made by dissolving litharge in a hot solution of an equivalent amount of lead nitrate. It crystallises well on cooling. Three other basic nitrates are prepared by the action of potassium nitrate on lead hydroxide, or of ammonia upon lead nitrate; the formulae of these are: $3\text{PbO} \cdot \text{N}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$; $10\text{PbO} \cdot \text{N}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$;

LEAD

$6\text{PbO} \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$. Strömholm obtained, further, a basic nitrate of the composition $4\text{PbO} \cdot \text{N}_2\text{O}_5$.

Basic Nitrites are produced by the hydrolysis of the normal nitrite; three have been described¹⁾, viz.: $2\text{PbO} \cdot \text{N}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$; $3\text{PbO} \cdot \text{N}_2\text{O}_3$ (hydrated), and $4\text{PbO} \cdot \text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

A *basic Azide* of the formula $\text{PbO} \cdot \text{PbN}_3$, has been prepared.²⁾

Basic Carbonates. The mineral hydrocerussite, $3\text{PbO} \cdot 2\text{CO}_2 \cdot \text{H}_2\text{O}$ has the same composition as the basic carbonate prepared by Hawley³⁾ and as the one produced in the white lead process. A more basic carbonate was isolated by Strömholm, viz.: $7\text{PbO} \cdot 4\text{CO}_2 \cdot \text{H}_2\text{O}$.

Basic Chromates. Four of these are known. The least basic, $2\text{PbO} \cdot \text{CrO}_3$ is the pigment Chinese Red or Chrome Red and is obtained by the action of an alkali on the normal chromate. The hydrate of this, $[\text{Pb}_2(\text{OH})_2]\text{CrO}_4$ is formed by the action of potassium chromate on the basic chloride $[\text{Pb}_3(\text{OH})_4]\text{Cl}_2$.⁴⁾ $3\text{PbO} \cdot \text{CrO}_3$ occurs as the mineral phenicite or phenicochroite; $5\text{PbO} \cdot \text{CrO}_3$ and $7\text{PbO} \cdot \text{CrO}_3$ were recognised by Jaeger and Germs in their study of the binary system of lead and chromic oxides. The former is unstable above 815° , the latter has a transition point at 774° and melts at 854° . The same authors recognise the existence of a basic molybdate $2\text{PbO} \cdot \text{MoO}_3$, m.p. 981° and a basic tungstate, $2\text{PbO} \cdot \text{WO}_3$, m.p. 899° .

Basic Perchlorates. By digesting 1 equivalent of litharge with from 1 to 2 equivalents of perchloric acid, a basic perchlorate, first prepared by Marignac, is obtained, having the formula 1). $\text{PbO} \cdot \text{Pb}(\text{ClO}_4)_2 \cdot 2.5\text{H}_2\text{O}$. With excess of litharge, the salt 2). $2\text{PbO} \cdot \text{Pb}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ separates from the hot solution. From these two salts, by double decomposition, a number of derivatives can be prepared, many of which

1 Chilesotti, *Atti R. Accad. Lincei*, 1908, [v] 17, [i] 824; [ii] 173, 288, 377, 474.

2 L. Wöhler and W. Kruppt, *Ber.*, 1913, 46, 2045.

3 *Journ. Phys. Chem.*, 1906, 10, 654.

4 Weinland and Stroh, *Ber.*, 1922, 55, 2706.

crystallise well and are stable enough to be recrystallised from hot water. The study of the chemical reactions and the electrical conductivity of these, by Weinland and Stroh¹), has led to the conclusion that they resemble, in many respects, the metal ammines, having a complex cation which though lacking the stability of the cations, say, of the cobaltammines, nevertheless persists unaltered during many chemical reactions.

Adopting the symbolism used in the case of the acetochlorates (p. 300), Weinland and Stroh represent compound 1). as $[\text{Pb}_2(\text{OH})_2](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$ and compound 2). as $[\text{Pb}_3(\text{OH})_4](\text{ClO}_4)_2$. From 1). the following compounds have been prepared by double decomposition with the alkali salt of the corresponding anion: 3). $[\text{Pb}_2(\text{OH})_2]\text{Cl}_2$; 4). $[\text{Pb}_2(\text{OH})_2](\text{NO}_3)_2$; 5). $[\text{Pb}_2(\text{OH})_2]\text{S}_2\text{O}_8$; 6). $[\text{Pb}_2(\text{OH})_2]\text{FeNO}(\text{CN})_5 \cdot \text{H}_2\text{O}$; and from 2). similar derivatives, with unchanged cation, viz.: 9). $[\text{Pb}_3(\text{OH})_4]\text{Cl}_2$; 10). $[\text{Pb}_3(\text{OH})_4]\text{I}_2$; 11). $[\text{Pb}_3(\text{OH})_4](\text{NO}_3)_2$; 12). $[\text{Pb}_3(\text{OH})_4]\text{S}_2\text{O}_8$.

With certain reacting salts, the cationic complex is altered, but the changes are obscure and nothing definite can be stated about the constitution of the resulting basic salts.

Thus 1). yields with potassium ferricyanide and potassium cobalticyanide the products: 7). $\text{Pb}_4(\text{OH})_2(\text{ClO}_4)_3\text{Fe}(\text{CN})_6$ and 8) $\text{Pb}_4(\text{OH})_2(\text{ClO}_4)_3\text{Co}(\text{CN})_6$ and 2) gives with ferricyanide the compounds 13). $\text{Pb}_5(\text{OH})_2(\text{ClO}_4)_2\text{Fe}(\text{CN})_6$ and 14). $\text{Pb}_5(\text{OH})_7\text{Fe}(\text{CN})_6 \cdot 3.5\text{H}_2\text{O}$; with cobalticyanide 15). $\text{Pb}_5(\text{OH})_8(\text{ClO}_4)_2\text{Co}(\text{CN})_6$ and with sodium nitroprusside 16). $\text{Pb}_4(\text{OH})_8(\text{ClO}_4)_4\text{FeNO}(\text{CN})_5 \cdot \text{H}_2\text{O}$.

Solution of basic lead acetate, when brought into action with the appropriate alkali salt yields compounds identical with 3) and 5) above, whence it may be argued that it contains a complex similar to that of the basic chloride 1). This shows

1 Ber. 1922, 55, 2219, 2706.

2 It will be observed that compound 3 is the same in composition as laurionite and Pattinson's white, and 4 as the first basic nitrate described above. There is no evidence to indicate complete identity of these compounds: it is conceivable that they may be isomeric.

a similar degree of instability, too, towards ferricyanide and cobalticyanide and gives rise to compounds of which the polar groupings are unknown, e.g. 17). $\text{Pb}_6(\text{OH})_7\text{Ac}_2\cdot\text{Fe}(\text{CN})_6\cdot\text{H}_2\text{O}$; 18). $\text{Pb}_4(\text{OH})_5\text{Fe}(\text{CN})_6$; 19). $\text{Pb}_4(\text{OH})_5\text{Co}(\text{CN})_6$.

Basic Lead Acetate. The facts detailed above throw some light on the nature of solutions of lead acetate. The normal salt contains water of crystallisation which, as Weinland and Stroh, remark, is uncommon in lead salts. Its concentrated solution is alkaline in reaction, whereas the dilute solution is acid; it shows certain analytical abnormalities and is much less ionised than are the solutions of other acetates.¹⁾ It yields basic acetate on dilution with water. The Liquor Plumbi Subacetatis of the British Pharmacopoeia is made by dissolving 2 equivalents of lead oxide in one of acetic acid and is nearly saturated: in very dilute solutions, however, as much as 10 equivalents of lead oxide can be dissolved by 1 of acetic acid. The basic salts which can exist as solid phases, in contact with the solution, are $\text{PbO}\cdot\text{PbAc}_2\cdot\text{H}_2\text{O}$ and $2\text{PbO}\cdot\text{PbAc}_2\cdot\text{H}_2\text{O}$.

Most of these properties stamp the acetate solutions of lead as molecularly abnormal. The existence in lead acetate solution of the polynuclear complex forming the cation $[\text{Pb}_2(\text{OH})_2]$ has already been inferred from its similarity in behaviour with Marignac's salt. Similar complexes are inferred in the case of the aceto-perchlorates, and there is complete correspondence between some of these and the basic perchlorates, e.g. $[\text{Pb}_2(\text{OH})_2](\text{ClO}_4)_2$ and $[\text{Pb}_2\text{Ac}_2](\text{ClO}_4)_2$; $[\text{Pb}_3(\text{OH})_4](\text{ClO}_4)_2$ and $[\text{Pb}_3\text{Ac}_3](\text{ClO}_4)_2$. There are grounds²⁾, therefore, for regarding lead acetate as containing the acetates of polynuclear lead acetato-cations and since solutions of lead acetate in water and acetic acid yield with perchloric acid the perchlorates of four polynuclear lead acetate cations, it may be inferred that these exist in acetate solutions, which therefore contain: $[\text{Pb}_2\text{Ac}_2]\text{Ac}_2$; $[\text{Pb}_2\text{Ac}_3]\text{Ac}$; $[\text{Pb}_3\text{Ac}_4]\text{Ac}_2$;

1 Noyes and Whitcomb, *Journ. Amer. Chem. Soc.*, 1905, **27**, 707.

2 Weinland and Stroh, *op. cit.*

$[\text{Pb}_4\text{Ac}_6]\text{Ac}_3$. Dilute solutions of the normal acetate and solutions of the basic acetate probably contain similar complexes, in which the acetic radicle is partly replaced by hydroxyl.

CHAPTER XIII.

LEAD POISONING

The poisonous effects of lead were described as early as the fifth century B.C. by Hippocrates and are mentioned by many of the old authors who have been quoted in connexion with the history of the metal. Not only was the swallowing of lead compounds recognised as dangerous, but also the inhaling of fumes in smelting operations; and the use of lead pipes for water supply, so common among the Romans, was condemned by Vitruvius on account of the risk of poisoning. The Romans tested the harshness of wine, by hanging a sheet of lead in it and examining its effects on the surface of the metal, and they also sweetened sour wine by boiling it in lead vessels¹), but they do not appear to have realised the danger of this practice. In the fifteenth century, lead or litharge was intentionally added to sour wine in order to sweeten it and the custom was so extended, and was attended with such disastrous results, that in France and Germany it had to be put down by legislation, the death penalty even being enacted.

These examples illustrate an important aspect of the subject, namely, that not only those engaged in the production of lead and its compounds, and those who use these in the arts, run the risk of poisoning, but the people in general are exposed to the danger, either by reason of the criminal intent or negligence of the few, or as the accidental result of the extensive employment of lead-bearing materials for so many of the purposes of daily life. Lead is a cumulative poison and the absorption of a minute quantity at a time, over a long interval, may produce disastrous results in the end. Its effects

¹ Pliny, *Hist. Nat. Lib.*, XIV., Cap. 20.

may thus be long in showing themselves and it is frequently a difficult matter to detect the source of the trouble and thus to prevent its widespread distribution. Well might Beckmann¹) exclaim, after contemplating the many possible methods and the frequency of lead-poisoning, "one may justly doubt whether, at present, Mars, Venus or Saturn is most destructive to the human race".

Plumbism or lead colic does not usually affect those who mine galena, but its incidence was severe at Broken Hill among the miners engaged in mining cerussite. Many of the operations of smelting are dangerous, notably barring down the furnace and tapping lead, matte and slag. The manufacture of white lead was for long a prolific source of plumbism and it is interesting to note in this connexion that Vernatti, seems to have realised the important part which dust plays in its causation, for it is generally recognised nowadays that gastro-intestinal and cutaneous absorption are quite subsidiary factors in industrial lead poisoning and, as Legge²) expresses it "all risk lies in the inhalation of dust and fume". Not only are those engaged in the manufacture of lead and its compounds liable to suffer from lead poisoning, but those, too, who use them in such industries as painting, printing, plumbing, file-cutting, enamelling and the glazing of pottery. The rate of attack, per 1000 employed, in some of these industries for the year 1910 was: tinning of metals, 34; making accumulators, 28; vitreous enamelling 22; white lead, 22; red lead 15; earthenware, 12; paints and colours, 11. Further statistics, showing the total number of cases and fatalities for the various industries in the United Kingdom, for the year 1911, are given in the table on page 309.³)

The symptoms of lead poisoning are pain in the abdomen, constipation, loss of appetite, thirst, a nervous prostration known as lead palsy, epileptic fits, and total paralysis. The

¹ *History of Inventions*, Vol. I, p. 345.

² *Ann. Rep. Chief Insp. of Factories*, 1918.

³ T. M. Legge and K. W. Goadby, *Lead Poisoning and Lead Absorption*, 1912.

| Cases of Lead Poisoning notified for the Year 1911 | | |
|--|-----------------------|-------------|
| Industry | Total Number of Cases | Fatal Cases |
| 1. Coach and Car Painting | 104 | 5 |
| 2. China and Earthenware | 92 | 6 |
| 3. Painting (exclusive of 1,7 and 10) . . | 56 | 1 |
| 4. Smelting of metals | 48 | 3 |
| 5. White Lead | 41 | 2 |
| 6. Plumbing and Soldering | 37 | 2 |
| 7. Shipbuilding | 36 | 6 |
| 8. Printing | 32 | 2 |
| 9. Electric Accumulators | 24 | 1 |
| 10. Paints and Colours | 21 | 0 |
| 11. Vitreous enamelling | 19 | 1 |
| 12. File-cutting | 18 | 2 |
| 13. Tinning of metals | 13 | 0 |
| 14. Red lead | 13 | 1 |
| 15. Sheet-lead and Lead-piping | 12 | 4 |
| 16. Brass Works | 9 | 1 |
| 17. Industries not specified in list | 8 | 0 |
| 18. Glass-cutting and Polishing | 5 | 0 |
| 19. Lithotransfers | 1 | 1 |
| Totals | 589 | 33 |

presence of a blue line at the edges of the gums was, until recently, considered to be a sign of lead poisoning. This line is however, not diagnostic; it is a secondary effect arising from a septic condition of the mouth and seldom occurs when the teeth are sound and the gums clean. It is only an indication that the person who shows it has, at some time or other, been subjected to lead absorption.

Susceptibility towards lead poisoning depends on many things. Women are more susceptible than men, and the under-fed are naturally more prone to attack than the well-nourished. Anaemia is one of the chief predisposing causes. Most people become tolerant of the poison to some degree, a certain balance being struck between absorption and secretion. This balance may be upset, with serious results, by the onset of disease or by a sudden increase in absorption. It was observed

that lead-workers, called up for the army during the great war, who then showed no signs of plumbism, were soon affected after their return to their old employment. Immunity is secured in such cases by re-adjustment of their tasks, so that dangerous works alternate with innocuous.¹⁾

Part of the lead taken into the system is excreted by the kidneys. The distribution of the metal in various organs of the body has been studied by Prof. Bedson, Sir D. Drummond and Sir T. Oliver, in the case of three lead-workers who succumbed to the poison, and their results are given in the table below. It will be noticed that the liver, in all cases, contained the greatest quantity of lead, but that the proportion relatively to the weight of the organ was greatest, in the one sample investigated, in the grey matter of the basal ganglia.

| Description of organ, &c. | Lead found expressed as metallic lead in parts per million | | | Lead in grains calculated on total weight of organ | | |
|--|--|------|------|--|--------|--------|
| | I. | II. | III. | I. | II. | III. |
| Large intestine . . . | 14.6 | 37.7 | — | — | — | — |
| Small intestine . . . | 9.2 | — | — | — | — | — |
| Muscle | 3.1 | — | — | — | — | — |
| Lung | 2.2 | 7.6 | — | — | — | — |
| Heart | 6.7 | 4.12 | 5.0 | 0.0243 | 0.0189 | 0.0164 |
| Mamma | 4.8 | — | — | — | — | — |
| Kidney | 15.5 | 10 | 13.3 | 0.027 | 0.0229 | 0.0261 |
| Spleen | 14.7 | 12 | 39.0 | 0.0193 | 0.0341 | 0.0853 |
| Liver | 47.7 | 37.8 | 41.6 | 0.918 | 1.000 | 0.728 |
| Cerebellum and pons | 36.9 | — | — | — | — | — |
| Grey matter of basal ganglia | 53 | — | — | — | — | — |
| Brain: grey matter of cortex | 40.9 | — | — | — | — | — |
| Brain: white substance | 18.9 | — | — | — | — | — |
| Spinal cord | — | 1.16 | — | — | — | — |
| Brain | — | 9.8 | 21.6 | 0.688 | — | — |
| Cerebellum | — | 24.8 | 8.59 | — | — | — |
| Pons | — | 22.6 | — | — | — | — |
| Brain and cerebellum | — | — | — | — | 0.779 | 0.634 |

¹ Sir K. Goadby, Reported in *The Times*, May 31, 1921.

The recognition of the danger of inhaling leady dust, especially when this is soluble in acid gastric juices, and of the general need of cleanliness in all operations and on the part of the work-folk, has been a potent factor in the development, during the last few decades, of measures for the safeguarding of the workers. A "lead process" is one in which the solubility of the material handled, as determined by Sir Edward Thorpe's method, (namely, by shaking 1 gram of the sample for 1 hour with 1 litre of 0.25 p.c. hydrochloric acid and allowing to stand 1 hour before estimating the lead in solution) is less than 5 p.c. Certain standard regulations are enforced for those who work with such materials, for example: a minimum age of worker, exclusion of women under 18 years of age, provision of messrooms, lavatories, overalls, medical inspection and a health register. All dusty operations are carried out with efficient exhaust ventilation.

There is a tendency, too, to centralise dangerous processes in large works, where effective means of avoiding danger are more readily provided, and to produce in these works intermediaries, rich in lead, but safe to handle with ordinary precautions. Thus, low-solubility silicates, containing 65 p.c. of lead, are safely made at lead works and can be used without danger for glazing in potteries; similarly, water pastes can be substituted for dry powders, and, in the rubber industry, thin sheets of rubber, containing 80 p.c. of lead compound, can be incorporated without difficulty with masses of rubber, thereby avoiding the use of dry powder at the rolls.¹⁾ Many modern developments, too, make for safety. Blast roasting of ores under hoods, or with exhaust, is advantageous, as is the smelting of highly desulphurised charges, with consequent low matte-fall, and the manufacture of white lead paste, by the wet-pugging process in the white lead industry is a notable case in point.

The effect of these measures is seen in the large falling off in the number of cases of plumbism notified. In 1900, no

¹ C. A. Klein, *Journ. Soc. Chem. Ind.*, 1922, 41, 325 R.

less than 1000 cases of industrial poisoning by lead were recorded in England; in 1922, the number had fallen to 200, though more lead was used. Among white lead-workers, the number of cases of poisoning was 399 in 1899, 13 years later it had decreased to 23, and in 1918, not a single case was recorded.¹⁾

Lead is used in medicine, as an astringent in diarrhœa and for its hæmastatic properties in gastric ulcer and hæmorrhage of the intestines: only the acetate is employed internally. For external use, the oleate, iodide and carbonate are valuable in ointments and plasters. All but three of the plasters in the British Pharmacopœia have lead oleate as a basis.

Statements concerning the effect of lead on the lower animals and on plants are curiously conflicting, owing possibly, to some extent, to the lack of precise knowledge as to the quantity of the metal concerned. Cattle are frequently poisoned (bellanded) in lead smelting districts, presumably in many cases by feeding on contaminated herbage, and yet it is stated that the Weardale shepherds fatten their sheep best in the neighbourhood of the smelting chimneys.²⁾ As the greater number of these have been out of use for many years, it is probable that most of the soluble lead compounds and the finer dust have been washed away, and possibly what remains has a stimulating effect upon the herbage. In this connexion, it has been shown that small quantities of lead nitrate have a stimulating effect on wheat, and that no toxic action is observable, even when the soil contains 0.03 p.c. of lead.

On the other hand, it has been shown that the lead washed down on to the arable lands of Cardiganshire from old-mine heaps has a detrimental effect on the crops; the leguminous ones suffer most, and the root crops sometimes absorb so much lead, that the cattle, feeding on them suffer

¹ For further information see Legge and Goadby, *op. cit.* Sir T. Oliver, *Lead Poisoning*, 1891; and *Dangerous Trades*, Ep. 19 (1902).

² F. C. Garrett and H. Garrett, *Nature*, 1922, 110, 380.

seriously.¹⁾ The poisonous effect of lead on weeds is well illustrated in the extensive use once made of the Bunter Conglomerate of Cannock Chase, which contains a cement carrying a little lead, for the mending of private walks and paths, and which was found inimical to the growth of weeds.²⁾

Certain low forms of life seem to thrive well in presence of lead. The nitrate has been shown to stimulate the growth of lepidopterous larvae³⁾ and earthworms were found to abound in an old waste bark heap from a white lead factory, at Elswick. This heap, which had accumulated for 50 years, averaged 2.5 p.c. of lead, reckoned as oxide, on the material dried at 100°. The intestines of the worms were full of the comminuted bark, the whole organism when dry containing 1.7—2.6 p.c. of lead as oxide; the amount of lead actually absorbed by the organs was 0.009—0.018 p.c. of their weight, which is greatly in excess of that found in any of the organs of human beings who have died of lead poisoning.⁴⁾

Finally, it may be mentioned that lead acts as a 'poison' towards many catalysts. The influence of the acetate on the catalytic activity of colloidal platinum, in the reduction of oleic acid with hydrogen, and on finely-divided platinum, in the decomposition of hydrogen peroxide, has been studied by Maxted, who finds that the activity of the catalyst is a linear function of the amount of lead present. It is argued from this that the catalyst is poisoned to an extent dependent on the quantity of lead, the remainder of the catalyst maintaining its full activity.⁵⁾

1 J. J. Griffith, *Journ. Agric. Soc.*, 1919, **9**, 366.

2 W. Molyneux, *Geol. Mag.*, 1873, **10**, 16.

3 F. C. Garrett and H. Garrett, *op. cit.*

4 T. W. Hogg, *Chem. News*, 1895, **71**, 223.

5 E. B. Maxted, *Journ. Chem. Soc.*, 1920, **118**, 1501; 1922, **122**, 1764.

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